Chemical Studies of the Western Pacific Ocean. IV. The Refractive Index of Sea Water.

By Yasuo MIYAKE.

(Received April 11, 1939.)

The refractive index of sea water was measured for the first time by J. Soret and Ed. Sarasin[1] in 1889. In 1900, H. Tornöe[2] studied the same subject and expressed the relation between salinity and refractive index by the next empirical formula:

$$\log n_D^{17.5}/S = 6.14340 - 0.00006 \cdot S ,$$

where n is the refractive index and S, the salinity. Apparently it seems possible to determine the salinity by applying this equation without resorting to the tedious volumetric method; however, it is to be regretted that the accuracy of the results thus obtained is far too inferior.

After Tornöe, attempts by O. Krümmel[3] and other later investigators in improving the new method to the state of practical application for determination of salinity proved fruitless. For instance, M. C. Vauraburg[4] obtained a convenient formula expressing the relation between refractive index and density of sea water at various temperatures, however, the accuracy of the results obtained by this formula barely approaches the order of that of an ordinary aerometer. In 1924, C. Pape[5] finally succeeded in the exact determination of salinity from the refractive index of water by measuring the minute differences between the refractive indices of standard water and samples with an interferometer of high precision. By this method, we can easily determine the salinity very precisely and in a few minutes. The chief object of the present work lies not in the determination of salinity but in a study leading to a stoichiometrical explanation of the refractive index of sea water.

Experimental. The Pulfrich's refractometer made by Fuess was used throughout the experiments. Sea water collected on March 16th, 1938 at N 42°38′, E 145°14′, was divided into ten samples of various chlorinities by dilution with water. The refractive index of each sample was carefully measured with Mazda's sodium lamp at 25°C. The results of the measurements are shown in Table 1.

As shown in Fig. 1, the relation between refractive index and chlorinity is almost linear and may be represented by the next empirical formula:

$$n_D^{25} = 1.33249_7 + 0.000334\,\mathrm{Cl} \qquad (1).$$

(1) J. Soret and Ed. Sarasin, *Compt. rend.*, **108** (1889), 1248.
(2) H. Tornöe, *Rep. Norw. Fish. Mar. Invest.*, **1** (1900), No. 6.
(3) O. Krümmel, "Handbuch der Ozeanographie", I, Stuttgart (1907).
(4) M. C. Vauraburg, *Compt. rend.*, **172** (1921), 863.
(5) C. Pape, *Ann. d. Hydrog.*, **53** (1924), 249; Schumacher, *Z. Ges. Erdk.* I, **47** (1926), 251.

Table 1. The Relation between Refractive Index and Chlorinity.

n	Cl‰	n	Cl‰
1.33863	18.54	1.33498	7.53
1.33812	16.73	1.33437	5.66
1.33742	14.80	1.33369	3.79
1.33681	13.07	1.33303	1.90
1.33629	11.23	1.33250	0.00
1.33559	9.37		

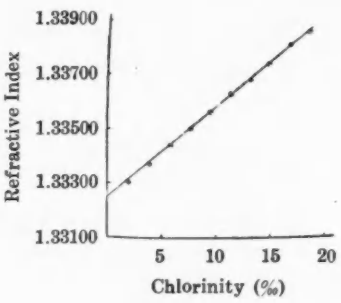


Fig. 1.

For the refractive index of pure water at 25°C., the average of the three values, 1.33251 (Hall and Payne), 1.33248 (Baxter and Burgess) and 1.33250 (measured by the author), was adopted.

The Refractive Index of Artificial Sea Water. It seems to be evident that the difference between the refractive index of pure water and sea water depends mainly upon the salts contained in the latter. It is of interest to know whether the refractive index of an artificial sea water is identical or not with that of a natural sea water of the same degree of chlorinity. An artificial sea water was prepared with chlorinity equivalent to 18.54‰ and its refractive index was measured. As shown in Table 2, the refractive index of the artificial sea water was in good agreement with that of natural sea water.

Table 2. A Comparison between the Refractive Index of Artificial and Natural Sea Waters of the same Chlorinity. Cl‰ 18.54.

Sea Water	Artificial	Natural
n_D^{25}	1.33863	1.33863.

In the next place, we may expect that when we dissolve the respective salts individually in water and measure the refractive index ν of each solution, the relation shown in the next formula should hold.

$$n = n_0 + \sum(\nu - n_0) \qquad (2),$$

where n is the refractive index of sea water; ν, the refractive index of each solution; n_0, the refractive index of distilled water.

Table 3 shows the results of the experiment.

Table 3.

Salt	g/l	ν	$\nu - n_0$
NaCl	26.4738	1.33707	0.00457
KCl	0.6922	1.33259	0.00009
$MgCl_2$	3.4112	1.33294	0.00044
$MgSO_4$	2.1825	1.33336	0.00086
$CaSO_4$	1.2838	1.33277	0.00027
$CaCO_3$	0.2170	1.33250	0.00000
			$\sum(\nu - n_0) = 0.00623$

$$n = n_0 + \sum(\nu - n_0) = 1.33250 + 0.00623 = 1.33873$$

$$n_{\text{observed}} = 1.33863 .$$

The results of the measurements described above, prove experimentally that the refraction of sea water is a summation of the individual refractions of pure water and dissolved salts. In the next paragraph, a more theoretical discussion will be given.

A Theoretical Consideration. Inasmuch as sea water is a dilute solution of inorganic salts, the greater part of each salt is dissociated into its ions. So, when refraction of sea water is mentioned, we must usually deal with the ionic refraction instead of molecular refraction. Therefore, since the values of the ionic refraction introduced from the theory of Lorenz-Lorentz have been calculated by Heydweiller[6] and K. Fajans,[7] we can easily obtain the equivalent refraction of sea water completely. According to the Lorenz-Lorentz's theory, the equivalent refraction (*E.R.*) of sea water is represented by the next formula:

$$E.R. = \frac{1000\,d}{d}\,\frac{n^2-1}{n^2+2} \qquad (3),$$

where n is the index of refraction of sea water and d, its density. On the other hand, *E.R.* is the sum of the refraction of pure water and of ions of the solute.

Then,

$$E.R. = \frac{1000\,d-S}{d_0}\,\frac{n_0^2-1}{n_0^2+2} + N_{Cl}R_{Cl} + N_{Na}R_{Na} + N_{SO_4}R_{SO_4} + N_{Mg}R_{Mg} + N_{Ca}R_{Ca} + N_K R_K \qquad (4),$$

where S is the quantity of salt per litre of sea water;
d_0, the density of pure water at 25°C.;
n_0, the refractive index of pure water at 25°C.;
N, the number of mols of each ion;
and R, the refraction of each ion.

(6) A. Heydweiller, *Ann. Physik*, **41** (1913), 499.
(7) K. Fajans and G. Joos, *Z. Physik*, **23** (1924), 1.

The first term of this formula is the refraction of pure water. Therefore, by knowing every N and R, we may completely evaluate the above formula.

In Table 4, the numerical values of N and R are given.

Table 4.

Ion	N mol/l	R c.c.	$N \times R$ c.c.
Na	0.4542	0.200	0.0908
Cl	0.5352	9.00	4.8168
SO_4	0.0276	14.63	0.4038
Mg	0.0541	−1.57	−0.0850
Ca	0.0108	0.68	0.0731
K	0.0093	2.23	0.0207
		Total	5.3202

The first term is;

$$\frac{1000\,d-S}{d_0}\,\frac{n_0^2-1}{n_0^2+2} = 203.533 \text{ c.c.}$$

where,

d, 1.022222 (25°C., Cl‰ 18.54);

d_0, 0.997069 (25°C.);

S, 34.26 g/l;

and

n_0, 1.33249$_7$ (25°C., Na D-line).

Then, the calculated value of $E.R.$ is;

$$E.R._{\text{calc.}} = 208.853 \text{ c.c.}\ .$$

On the other hand the value of $E.R.$ obtained from Formula (3) becomes;

$$E.R._{\text{obs.}} = 208.846 \text{ c.c.} \qquad (n = 1.33863).$$

The two results are in quite good agreement. Thus we have been able to demonstrate theoretically that the refraction of sea water is a sum of the refractions of pure water and of solute ions.

It is interesting to note that 90% of the ionic refraction is due to the chloride ion. There is a parallelism between molecular refraction and molecular volume; probably in this case, the chloride ion may be the one which occupies the largest space in sea water.

Summary.

(1) Refractive indices of sea water of various chlorinities were measured and the following empirical formula was obtained:

$$n_D^{25} = 1.33249_7 + 0.000334\,\text{Cl}$$

(2) An assumption that the refraction of sea water is a summation of the individual refractions of pure water and dissolved salts, was proved both experimentally and theoretically.

In conclusion, the author wishes to express his hearty thanks to Prof. T. Okada, Director of the Central Meteorological Observatory of Japan, for his kind guidance and the permission of publishing this report. He is also indebted to Mr. H. Matui for his earnest assistance throughout this work.

Central Meteorological Observatory of Japan.

Studies on the Effect of Electric Field on the Viscosity of Liquids.

By Osamu KIMURA.

(Received April 19, 1939.)

Introduction. Many experiments have been done on the effect of electric field on the viscosity of liquids,[1] but few, on the viscosity of solutions.[2] This paper deals with the effect of electric field on the viscosity of the following solutions. As the solutes, a homologous series of fatty acids (lauric, myristic, palmitic, and stearic acids) and an alcohol (cetyl alcohol) were used. In this homologue the number of carbon of an acid increases from the next lower one by two, or the length of the molecule increases regularly according to the number of carbon of acid. While this electro-viscose effect seems to depend upon the length of the molecule of solute, and if so, it is interesting to examine how this effect depends upon the length of molecule of solute. For this purpose the homologue of fatty acid is selected here. As the solvents, benzene and hexane, both of which are non-polar and show no electro-viscose effect, were used. The author reports here the results of the measurement, using special viscosimeter, of the viscosity of solutions which are prepared by combining these solutes and solvents. One of these solutions, i.e. benzene solution of stearic acid has been investigated and reported in the previous paper.[3]

Apparatus. The author has devised for this experiment a special viscosimeter which is similar to that of L. Herzog and S. Sokolow.[1] The principle of measurement is the same as Ostwald's viscosimeter, but the modified capillary part in applying electric field, is composed of two pieces of electrodes, of which the gap is very narrow and has rectangular section. The whole apparatus is shown in Fig. 1 and the section of the capillary part, in Fig. 1a. As we see in the figure, the apparatus is composed of three parts, i.e. glass bulb A, capillary C and the glass tube B. The volume of A is about 2 c.c. The electrodes are made of aluminium block, the surface of which is covered by electrolytic oxide film in order to make it a good insulator of electricity. Between two electrodes, two thin pieces of glass are inserted. Then we get a capillary of rectangular section, the dimension of which is 0.3×0.02 cm.^{2}, and the length of capillary is

(1) W. Krönig, *Wied. Ann.*, **25** (1885), 618. W. Duff, *Phys, Review*, **1896**, 23. G. Quincke, *Wied. Ann.*, **62** (1897), 1. Q. Pacher and L. Finazzi, *Atti, Re 1st Ven.*, **59**, 2 (1889-1900), 389. A. Pocchottino, *Atti. D. Real. Accad. dei Linc.*, V. **12**, 2 (1903), 389. Ercollini, Il. Nuovo Cimento, **5** (1903), 249. Ph. Lenard, *Ann. Physik.*, (4) **61** (1920), 715. R. Herzog, H. Kudar, and E. Paersch, Naturwissenschaften, **21** (1933), 622., *Physik. Z.*, **35** (1934), 466. E. D. Alock., *Physics*, **7** (1936), 126. Y. Björnståhl, *Physics*, **6** (1935), 257. S. Dobinski, *Physik. Z.*, **14** (1935), 509. P. Sokolow and S. Sosinski, *Acta Physicochimica*, U.R.S.S., **5** (1936), 433, 691., *Ber. Akad. U.R.S.S.*, **4** (1935), 123.

(2) A. Passynski, *Kolloid-Z.*, **70** (1935), 180. Y. Björnståhl and K. O. Snellman, *Kolloid-Z.*, **78** (1937), 258.

(3) O. Kimura, this Bulletin, **12** (1937), 147.

6 cm. It is naturally very important to keep the apparatus at constant temperature as the viscosity of liquid is much affected even by a slight fluctuation of temperature. For this purpose, the apparatus must be set up in a thermostat. Since the liquid thermostat is inconvenient, the author has preferred air thermostat, of which the fluctuation of temperature is below 0.1°C. The time is measured by a stop-watch, which is accurate to one tenth of a second. The source of high voltage electricity is obtained by the usual means of a step up A.C. 100 volt transformer and rectifying it to direct current.

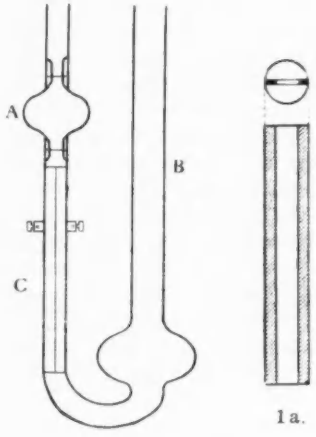


Fig. 1.

Table 1.

Solvent	Solute	Molar fraction	Gram %
benzene	lauric acid	0.01	2.272
,,	,,	0.02	4.591
,,	,,	0.04	9.393
,,	myristic acid	0.01	2.590
,,	,,	0.02	5.233
,,	,,	0.04	10.69
,,	palmitic acid	0.01	2.909
,,	,,	0.02	5.877
,,	,,	0.04	12.00
,,	stearic acid	0.01	3.227
,,	,,	0.02	6.520
,,	,,	0.04	13.32
,,	cetyl alcohol	0.01	2.750
,,	,,	0.02	5.557
,,	,,	0.04	11.34
hexane	,,	0.04	11.72

Experiment. The solvents, benzene and hexane, were first purified and then dried by distilling them over pieces of sodium. Lauric acid and cetyl alcohol are of Takeda's pure chemical, and stearic, palmitic, myristic acid are of Merck's. As the unit of concentration, molar fraction is used. The determination was done in all cases on the solution of following three concentrations, namely; 0.01, 0.02, 0.04. The relation of molar fraction with gram percent is shown in Table 1. The temperature is kept at 20°C. throughout the experiment. The measurement of viscosity was proceeded first from pure benzene and hexane. These non-polar solvents did not show any change of viscosity in electric field, as found by the earlier investigators. Then the measurement was carried out on the above-mentioned solutions. In this case, the increase of viscosity occurs when the electric field is applied, and the reproducibility of this effect has been checked by the successive observations of the time of transpiration with or without electric field. The applied voltage varies from zero to thousand volts. The voltage per centimeter may hardly be calculated as the distribution of potential in oxide film is unknown. Therefore here is described only the applied voltage. As the distance of electrode is 0.02 cm., if we assume

the layer of oxide film very thin, the approximate voltage can be estimated by multiplying the applied voltage by 50.

The movement of liquid in a capillary tube of rectangular section is calculated by Rowell and Finlayson,[4] that is

$$Q = \frac{4}{3} \cdot \frac{H}{\eta} \cdot bh^3 \left(1 - x \cdot \frac{h}{b}\right) t$$

$$\text{where} \quad x = \frac{192}{\pi^5} \cdot \sum_{n=1}^{n=\infty} \left(\frac{1}{n^5} \cdot \tanh \frac{\pi n b}{2h} \right) \quad \text{with } n \text{ odd},$$

and Q is the volume of the transpirated liquid in t seconds, the viscosity, b and h two sides of rectangle, H pressure, x number only referring to b and h. In this apparatus since Q, H, b and h are constant, we can get the following relation;

$$\eta \propto t$$

This is the same as found in Ostwald's viscosimeter, therefore we can assume that the time of transpiration is proportional to viscosity.

Now the results are shown in Tables 2–7 and Figs. 2–6.

Table 2. Lauric acid ($C_{11}H_{23}COOH$) in benzene.

Concentration	Voltage	t''	$\frac{\Delta t}{t} \times 100$
0.01	0	48.2	0.00
,,	300	48.2	0.00
,,	400	48.3	0.21
,,	500	48.4	0.42
,,	600	48.5	0.62
,,	700	48.6	0.83
0.02	0	47.3	0.00
,,	300	47.4	0.21
,,	500	47.5	0.42
,,	600	47.6	0.63
,,	700	47.7	0.85
,,	800	47.8	1.06
0.04	0	51.0	0.00
,,	300	51.1	0.20
,,	400	51.2	0.39
,,	500	51.3	0 59
,,	600	51.4	0.78
,,	700	51.5	0.98
,,	800	51.6	1.18

Table 3. Myristic acid ($C_{13}H_{27}COOH$) in benzene.

Concentration	Voltage	t''	$\frac{\Delta t}{t} \times 100$
0.01	0	68.4	0.00
,,	300	68.4	0.00
,,	400	68.5	0.15
,,	500	68.6	0.29
,,	600	68.7	0.44
,,	700	68.8	0.59
,,	800	69.0	0.88
0.02	0	49.6	0.00
,,	200	49.7	0.20
,,	300	49.8	0.40
,,	400	50.0	0.81
,,	500	50.3	1.41
,,	600	50.5	1.82
,,	700	50.8	2.42
,,	800	51.2	3.23
0.04	0	55.3	0.00
,,	300	55.5	0.36
,,	400	55.7	0.72
,,	500	56.1	1.44
,,	600	56.5	2.17
,,	700	56.9	2.89
,,	8.0	57.3	3 62
,,	900	58.0	4.88

(4) *Engineering*, **126** (1928), 249, 385., see also G. Barr, "A Monograph of Viscometry", 145, (1931).

Table 4. Palmitic acid ($C_{15}H_{31}COOH$) in benzene.

Concentration	Voltage	t''	$\frac{\Delta t}{t}\times 100$
0.01	0	47.7	0.00
,,	100	47.8	0.21
,,	200	48.9	0.42
,,	300	49.0	0.63
,,	500	49.1	0.84
,,	600	49.1	0.84
,,	800	49.1	0.84
0.02	0	55.1	0.00
,,	150	55.2	0.18
,,	300	55.3	0.36
,,	500	55.4	0.54
,,	800	55.5	0.73

The solution of 0.04 molar fraction cannot be obtained due to its solubility restriction.

Table 5. Stearic acid ($C_{17}H_{35}COOH$) in benzene.

Concentration	Voltage	t''	$\frac{\Delta t}{t}\times 100$
0.01	0	48.2	0.00
,,	300	48.3	0.21
,,	500	48.4	0.42
,,	800	48.4	0.42
0.02	0	49.7	0.00
,,	200	49.9	0.40
,,	300	50.1	0.80
,,	400	50.2	1.01
,,	500	50.3	1.21
,,	600	50.3	1.21
,,	700	50.3	1.21
,,	800	50.3	1.21
0.04	0	61.7	0.00
,,	100	62.0	0.49
,,	200	62.5	1.30
,,	300	64.2	4.05
,,	400	65.0	5.35
,,	500	65.0	5.35
,,	600	65.0	5.35
,,	700	65.0	5.35
,,	800	65.0	5.35

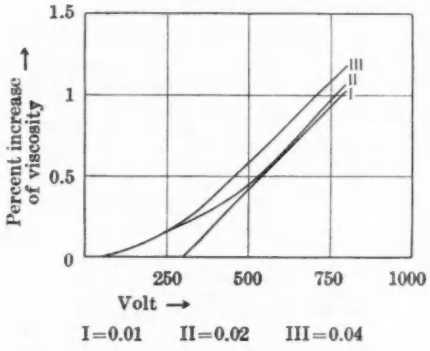
Table 6. Cetyl alcohol ($C_{15}H_{31}CH_2OH$) in benzene.

Concentration	Voltage	t''	$\frac{\Delta t}{t}\times 100$
0.01	0	45.0	0.00
,,	300	45.1	0.22
,,	500	45.2	0.44
,,	600	45.2	0.44
,,	700	45.2	0.44
,,	800	45.2	0.44
0.02	0	48.6	0.00
,,	100	48.7	0.21
,,	200	48.9	0.62
,,	300	49.1	1.03
,,	500	49.1	1.03
,,	800	49.1	1.03
0.04	0	54.5	0.00
,,	100	55.9	0.73
,,	200	56.8	2.39
,,	300	57.3	5.14
,,	400	57.4	5.32
,,	500	57.4	5.32
,,	550	57.8	6.05
,,	600	58.2	6.78
,,	700	58.5	7.34
,,	800	58.5	7.34
,,	800	58.9	8.08
,,	900	59.3	8.80
,,	1000	60.0	10.10

Table 7. Cetyl alcohol in hexane.

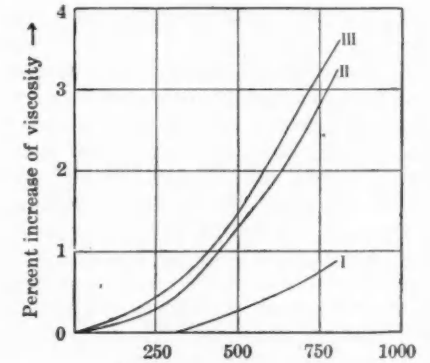
Concentration	Voltage	t''	$\frac{\Delta t}{t}\times 100$
0.04	0	41.0	0.00
,,	100	41.1	0.93
,,	200	42.2	2.93
,,	300	42.2	3.42
,,	400	42.4	3.42
,,	500	42.4	3.42
,,	600	42.4	3.42
,,	650	42.4	3.42
,,	700	42.7	3.14
,,	750	42.7	3.14
,,	800	42.8	4.39
,,	850	42.9	4.64
,,	900	43.1	5.12

In the earlier experiments, the remarkable electro-viscose effect was observed when the liquid touches electrodes directly; and little effect was observed when the liquid is insulated from electrode, say by glass layer. This is partially due to the enormous drop of voltage in glass layer, and partially to the movement of ion in liquid. In fact, Sokolow[1] proved that this effect remarkably depends upon the conductivity of liquid, while electrolysis occurs at the same time when the liquid touches electrode directly, and may have some influences. Accordingly, in this case, the phenomenon is too complicated to give the proper interpretation. Therefore to minimize such disturbing influences it is necessary to insulate liquid from electrodes. It is for this reason that in the experiment the electrode was covered by oxide film to insulate it from liquid. The result of experiment clearly shows that in general the viscosity increases with voltage, but the way of increase is characteristic in each solution. This result is remarkable, considering that these substances are homologue. First, in the case of lauric acid, in which the number of carbon is least; the increase of viscosity is less noticeable than others, and is in linear relation with voltage. Next, in myristic acid in which the number of carbon is two more than that of lauric acid, the nature of curve is almost the same, but the increase is more noticeable. Although palmitic acid comes next, let us first take up the case of stearic acid. The form of curve is quite different, and viscosity increases proportionally with the increase of electric field so long as it is weak, but when it reaches a certain limiting value, the viscosity no



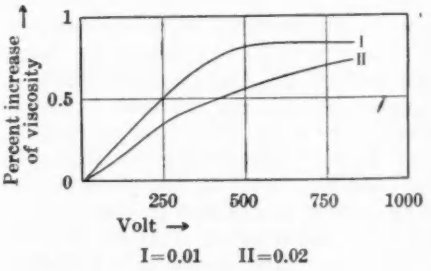
I=0.01 II=0.02 III=0.04

Fig. 2. Lauric acid in benzene.



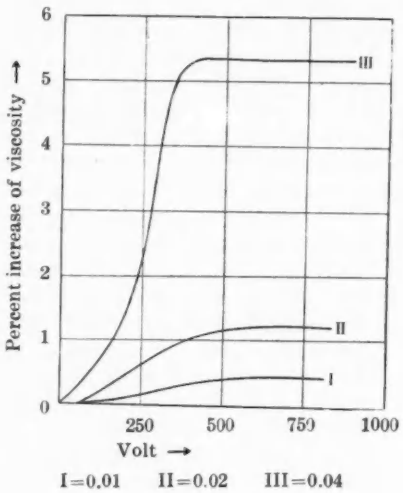
I=0.01 II=0.02 III=0.04

Fig. 3. Myristic acid in benzene.



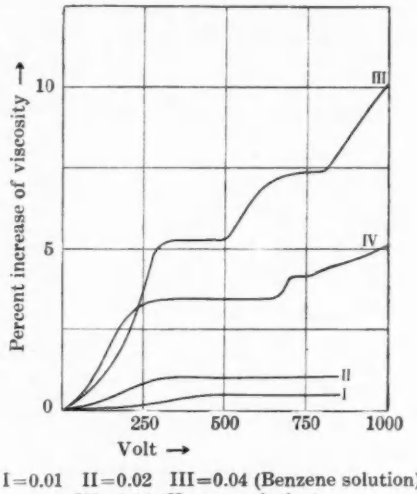
I=0.01 II=0.02

Fig. 4. Palmitic acid in benzene.



I=0.01 II=0.02 III=0.04

Fig. 5. Stearic acid in benzene.



I=0.01 II=0.02 III=0.04 (Benzene solution)
IV=0.04 (Hexane solution)

Fig. 6. Cetyl alcohol in benzene and hexane.

longer increases. This phenomenon is common in three different concentrations. The break point in the curves practically coincides with one another. Now let us consider palmitic acid, which lies between myristic and stearic acid in their number of carbon. The nature of curve again seems to be similar with those of two acids and lie between those of two acids. Now the curve of cetyl alcohol is the most characteristic as compared to the rest; in this case, as we see in the figure, the viscosity increases stepwise, and in the horizontal part of the curve for benzene solution corresponds with that of hexane solution, which shows that electroviscose effect is almost independent of the nature of solvent. Thus we can say that in homologue series, the longer the molecule of solute and the more concentrated a solution is, the greater the effect appears.

In general, if the solute has a dipole moment, the electric field will tend to orient the solute molecule in a direction which is parallel to the field. If F be the field strength and μ the electric dipole moment of the molecule, the energy of the molecule due to the electric field will be $\mu F\cos\alpha$, where α is the angle between the dipole axis and the direction of the electric field. There are also thermal energy and energy due to viscous flow associated with molecule. Thermal energy does not depend upon angle between the dipole axis and the direction of the electric field, hence it will cause no orientation of the molecules. Neglecting the viscous stress, we can compare the magnitude of electrical energy with that of thermal energy, as mentioned in the previous paper,[3] and obtain the following result that the number of molecules, which orients to the direction of electric field, is very few at the voltage which is realized in this experiment, and so if we raise the field intensity, the number of oriented molecules must increase, and also the viscosity. The above interpretation agrees with experimental results of lauric and myristic acids, and the

results for palmitic acid slightly deviates from the theory, while in stearic acid much more deviation is observed; hence it may be stated that longer the chain, the greater the deviation. This suggests us that the phenomenon may be influenced by some other additional factors. It is more complicated in the case of cetyl alcohol. The reason of this descrepancy from the theory is that the above-mentioned assumption is too simple to be applied in this case. The association of the molecule of solute may be an explanation. The fact that the greater the molecular weight, the easier to form associated molecules, agrees with these experimental results; and that in the case of cetyl alcohol the effect is independent of solvent also supports this theory.

Summary.

(1) A capillary viscosimeter is made, to which electric field can be applied.

(2) By means of this viscosimeter, the viscosity of benzene and hexane solution of lauric, myristic, palmitic, and stearic acid and of cetyl alcohol is measured in the presence of electric field.

(3) The viscosity of these solutions generally increases in electric field, and the stronger the field the greater the increase. The acid with longer chain shows much more effect than one with the shorter. In a solution the effect is proportional to concentration.

(4) In lauric acid, the increase of viscosity shows a linear relation. In stearic acid, the increase ceases at a certain voltage.

(5) In cetyl alcohol the viscosity increases stepwise and the form of the viscosity-field intensity curve is independent of the nature of solvent.

(6) This electro-viscose effect is due to the orientation of molecules of solute.

(7) The irregularity of curves in stearic acid and cetyl alcohol seems to be the result from association.

In conclusion, the author wishes to express his sincere gratitude to Professor N. Sata who has been kind enough to give him guidance and encouragement throughout this research.

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On the Nature of Foam. VI. Emulsion and Foam Formation of Ternary System, Ethyl Alcohol—Ethyl Ether—Water.

By Tunetaka SASAKI.

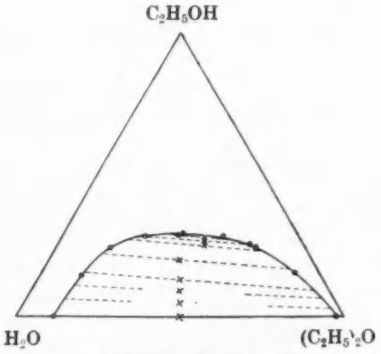
(Received April 24, 1939.)

It was indicated in the preceding papers[1][2] that in ternary systems of acetic acid–ethyl ether–water (AEW) and acetic acid–benzene–water (ABW), the diagram showing the relation between foam formation and composition has two maxima, one of which being situated in the region where the system shows critical opalescence or anomalous viscosity. In the case of ternary system of ethyl alcohol–ethyl ether–water (EEW), however, it has been known that there exists no region of such critical opalescence.[3] It is interesting, therefore, to investigate whether this system has or lacks the maximum of foam formation corresponding to the absence of critical opalescence. Present paper describes the foam formation and the nature of emulsion of EEW-system.

Experiments. In ternary system of EEW, ethyl alcohol is soluble in all proportions both in ether and in water, while ethyl ether is hardly miscible with water. The mutual solubility curve of this system was obtained by the measurements of volume compositions of limiting turbid mixtures.[1] The data and the diagram are shown in Table 1 and in Fig. 1. Tie-lines were determined from a volume ratio of upper and lower

Table 1.

Volume composition of limiting turbid mixture (c.c.)		
Ethyl alcohol	Ethyl ether	Water
0	1.15	8.85
0	9.80	0.20
1.45	1.30	7.25
1.55	7.75	0.70
2.40	1.59	6.01
2.45	6.12	1.43
2.52	5.90	1.58
2.81	2.52	4.67
2.81	4.93	2.26
2.88	3.52	3.60
2.92	3.66	3.42



⊙ System of Table 1.
× System of Table 2.

Fig. 1.

(1) Sasaki, this Bulletin, **13** (1938), 669.
(2) Sasaki, this Bulletin, **14** (1939), 3.
(3) Sata and Kimura, this Bulletin, **10** (1935), 409.

liquid layers (V_u and V_l respectively) coexisting in a heterogeneous system, as described in the preceding paper.[1] The data are shown in Table 2 and are also depicted in Fig. 1.

Table 2.

Composition in volume (c.c.)			Volume ratio	
Ethyl alcohol	Ethyl ether	Water	Upper layer	Lower layer
0	5.00	5.00	0.818	1.000
0.48	4.76	4.76	0.763	1.000
0.90	4.55	4.55	0.742	1.000
1.30	4.35	4.35	0.707	1.000
2.00	4.00	4.00	0.700	1.000
2.50	4.50	3.00	1.334	1.000
2.65	4.41	2.94	1.390	1.000
2.79	4.33	2.88	1.630	1.000

The measurements of the foam stability were then undertaken for homogeneous and heterogeneous systems of EEW, using the same shaking apparatus and on the same conditions as described in the preceding paper.[1] A constant volume (10 c.c.) of liquid for measurement is introduced in a test tube of 1.5 cm. in diameter and 15 cm. in length, and is shaken 300 times for 10 seconds with amplitude of 12 cm. The time required from immediately after the stop of shaking to the complete collapse of foam zone was measured and was considered to be the stability of foam. The height of foam was not measured for the sake of simplicity. Some of the results of measurements are shown in Table 3, the data of which are shown diagramatically in Fig. 2.

Table 3.

Composition in volume (c c.)			Stability of foam (second)	Composition in volume (c.c.)			Stability of foam (second)
Ethyl alcohol	Ethyl ether	Water		Ethyl alcohol	Ethyl ether	Water	
0	1.15	8.85	0	2.60	3.70	3.70	1.3
0	9.80	0.20	0	2.70	3.10	4.20	0
0.25	0	9.75	6.1	2.86	2.80	4.34	0
0.50	0	9.50	7.3	2.90	3.40	3.70	1.8
0.50	0.50	9.00	2.2	2.90	3.70	3.40	0
0.50	1.00	8.50	1.7	2.90	5.10	2.00	3.1
0.98	1.22	7.80	1.8	3.00	2.00	5.00	10.6
1.00	0.50	8.50	4.6	3.00	2.50	4.50	17.9
1.20	5.80	3.00	0	3.00	3.00	4.00	36.9
1.50	0	8.50	3.9	3.00	3.50	3.50	22.4
1.50	1.00	7.50	1.8	3.00	4.00	3.00	22.2
1.50	7.00	1.50	1.2	3.00	4.50	2.50	6.8
1.90	1.40	6.70	0	3.50	0	6.50	2.6
2.00	0.50	7.50	2.3	3.50	3.00	3.50	4.2
2.00	1.00	7.00	8.9	3.50	3.80	2.70	3.0
2.00	5.50	2.50	1.4	4.00	1.00	5.00	2.6
2.20	3.90	3.90	0.5	4.50	3.00	2.50	1.5
2.50	1.00	6.50	2.9	5.00	5.00	0	0
2.50	4.50	3.00	1.7	6.00	2.00	2.00	0.5
2.50	6.00	1.50	2.6	7.50	2.50	0	0
2.50	7.50	0	0				

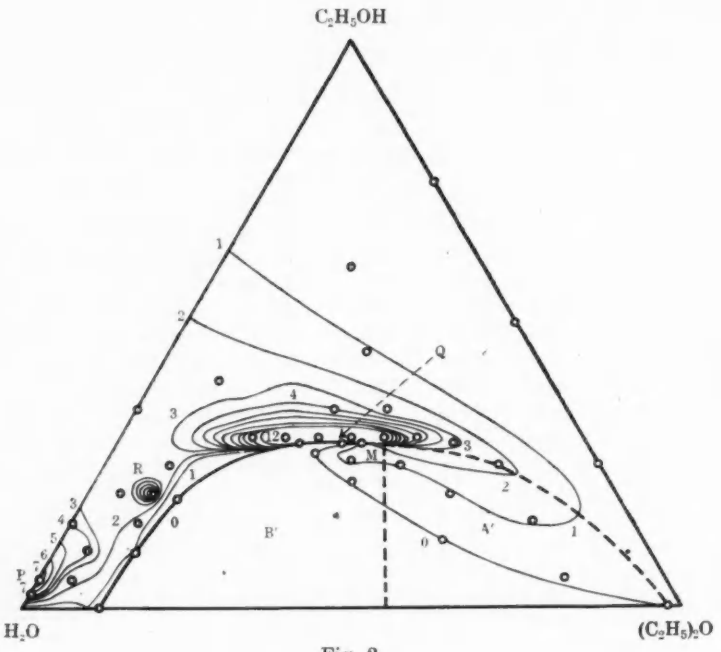


Fig. 2.

An emulsion produced by a system belonging to the heterogeneous region of EEW also exhibits characteristic behaviours according to the different modes of shaking as described in the preceding papers.[4][5] So it was further investigated precisely. A definite volume (10 c.c.) of this heterogeneous system is taken in a test tube and the following two modes of shaking are applied to it.

(1) The test tube is held vertically by hand, pulled upwards quickly and then brought down slowly. After repeating these motions several times, it is shaken up and down in usual manner.

(2) The upper portion of the test tube is held vertically by hand, and the lower portion of it is swung several times. Usual up-and-down shaking is subsequently applied.

The type of emulsion thus produced is determined by the appearance of breaking up of emulsion as shown in the preceding paper,[4] namely, emulsion is considered to be oil in water (O-in-W) type when drops of disperse phase increase their size as they go upwards and gradually separate themselves as a liquid layer upon the bulk, while it is considered to be water in oil (W-in-O) type when drops of disperse phase increase their size as they sink and gradually separate themselves as a liquid layer at the bottom. Thus, the type of emulsion produced in various heterogeneous systems of EEW were determined. Some of the

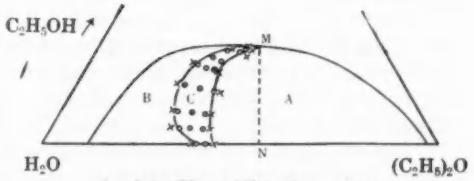
(4) Sasaki, this Bulletin, **14** (1939), 63.
(5) Sasaki, this Bulletin, **14** (1939), 107.

Table 4.

Composition in volume (c.c.)			Type of emulsion produced by shaking of the mode	
Ethyl alcohol	Ethyl ether	Water	(1)	(2)
2.90	3.70	3.40	O-in-W	O-in-W
2.80	3.40	3.80	O-in-W	O-in-W
2.79	3.75	3.46	O-in-W	W-in-O
2.75	3.30	3.95	O-in-W	W-in-O
2.71	3.93	3.36	W-in-O	W-in-O
2.70	3.65	3.65	O-in-W	W-in-O
2.59	3.89	3.52	W-in-O	W-in-O
2.55	3.04	4.41	O-in-W	W-in-O
2.45	3.30	4.25	O-in-W	W-in-O
2.40	2.60	5.00	O-in-W	O-in-W
2.35	2.75	4.90	O-in-W	W-in-O
2.18	3.27	4.55	O-in-W	W-in-O
2.14	3.39	4.47	W-in-O	W-in-O
1.80	2.50	5.70	O-in-W	O-in-W
1.75	2.72	5.53	O-in-W	W-in-O
1.54	3.59	4.87	O-in-W	W-in-O
1.50	3.75	4.75	W-in-O	W-in-O
1.00	2.80	6.20	O-in-W	O-in-W
0.98	2.94	6.08	O-in-W	W-in-O
0.88	3.68	5.44	O-in-W	W-in-O
0.86	3.84	5.30	W-in-O	W-in-O
0.50	3.00	6.50	O-in-W	O-in-W
0.48	3.27	6.25	O-in-W	W-in-O
0.44	3.86	5.70	O-in-W	W-in-O
0.43	4.02	5.55	W-in-O	W-in O
0	4.35	5.65	W-in-O	W-in-O
0	4.12	5.88	C-type*	W-in-O
0	3.86	6.14	C-type*	W-in-O
0	3.75	6.25	O-in-W	O-in-W

* Complex type i.e. the upper layer is W-in-O type and the lower layer, O-in-W type.

results are shown in Table 4. These data are depicted in Fig. 3. In this figure, A and B represent the region in which systems show only one type of emulsion, W-in-O and O-in-W types respectively, whatever the modes of shaking, and C represents the region in which systems show the tendency to produce both types of emulsions according to the above two modes of shaking.



○ O-in-W or W-in-O system.
× Phase inversion system.

Fig. 3.

In the phase inversion zone, a series of systems, varying in volume ratio of upper and lower liquid layers of nearly definite compositions respectively, were investigated in order to see the effect of volume to the nature of emulsion produced by shaking. In this measurements, 10 c.c. of a system is taken in a test tube and the following three modes of shaking are applied to it.

(1) The mode of shaking described in (1) of Table 4.
(2) The mode of shaking described in (2) of Table 4.
(3) Usual up-and-down shaking only is applied from the beginning.

The type of emulsion produced by above three modes of shaking are determined from the behaviours of breaking up of emulsion in the same manner as described before. The stability of emulsion, that is, the time required from immediately after shaking to the complete collapse of emulsion droplets, was also measured. The results are shown in Table 5.

Discussion. The diagram of the foam stability of EEW-system, as a whole, is similar in the shape to that of ABW-[2] and especially to AEW-system.[1] In the homogeneous region, surface of the diagram is steep along ethyl alcohol–water line and particularly the steepest along a portion of mutual solubility curve, while it has a gentle slope towards ethyl ether–ethyl alcohol line. The stability of foam shows maxima at three points P, Q and R in Fig. 2. Point P corresponds to the maxima of foam stability of binary mixture, ethyl alcohol–water, which has already been determined from the measurement of foam stability by another method.[6] The maximum point Q is situated along the mutual solubility curve and the degree of stability at this point far more exceeds that at P. These relations are quite similar to AEW-system.[1]

It was suggested in AEW-[1] and especially in ABW-system[2] that such region of remarkable foam stability and the region of critical opalescence or anomalous viscosity take the same position. Such regions are also near the point of intersection (M in Fig. 2) made by the mutual solubility curve and the locus of middle points of tie-lines. In the heterogeneous system near this point, the physical properties of upper and lower liquid layers closely resemble each other and the system shows the nature of colloidal solution when shaken. The maximum of foam formation as well as critical opalescence and anomalous viscosity was explained from this colloidal nature in the preceding papers.[1][2] In the present case of EEW-system, the foam stability shows its maximum at point Q, although it is known that critical opalescence is absent in this system.[3] The point Q is also situated in the vicinity of the point of intersection (M) made by the mutual solubility curve and the locus of middle points of tie-lines. Maximum of foam stability can also be seen at point R, but it is rather uncertain as the vicinity of this point was not precisely investigated.

The diagram of foam stability in the heterogeneous region of EEW-system, like that of AEW-system, consists of two parts, foamy and non foamy regions which are represented as A′ and B′, respectively, in Fig. 2.

(6) Sasaki, this Bulletin, **13** (1938), 517.

In a heterogeneous system of A′ region, foam can be produced on shaking, because a lower liquid layer of larger surface tension and smaller volume is dispersed in an upper one, and the foam formation was not prevented by these emulsion drops as was described in the preceding paper.[1] In a heterogeneous system of B′ region, an upper liquid layer of smaller surface tension and smaller volume is dispersed in a lower one on shaking.[1] In such conditions, the film of foam is destroyed by emulsion droplets and the system does not foam on shaking. Frequently, emulsion droplets containing air bubbles are obtained on shaking in the case where emulsion droplets have considerably smaller surface tension than the dispersing medium as in the case of AEW-system.

The heterogeneous region is divided into three portions A, B and C, referring to the type of emulsion produced by shaking as shown in Fig. 3. In a heterogeneous system of A region, the upper liquid layer is generally excessive in volume compared with the lower one and the system shows the tendency of the lower layer being dispersed in the upper one, namely, W-in-O emulsion results whatever the modes of shaking.[4] A heterogeneous system of B region, in the same manner, shows the tendency of the upper layer being dispersed in the lower one and O-in-W emulsion results, independent of the modes of shaking. The region A also involves systems in which a lower layer is slightly excessive in volume than the upper one, and yet the former is dispersed in the latter. The system of C region shows the tendency of producing both types of emulsion according to the two different modes of shaking. The modes of shaking described in (1) favours to produce O-in-W emulsion and the shaking of the mode (2) favours to produce W-in-O emulsion. These relations between mode of shaking and type of resulting emulsion is similar to those of AEW- and ABW-systems, and they can also be explained in the same manner.[4] The region C is also called the zone of phase inversion by shaking. It can be seen that this zone of phase inversion is not situated along the line MN. It is not necessary for the phase inversion system that volumes of upper and lower layers are equal, as in the case of AEW-[4] and ABW-systems.[5] The behaviours of a system belonging to the zone of phase inversion was precisely studied and are tabulated in Table 5. It can be seen in this table that the behaviours of phase inversion systems to the shaking gradually change with relative volume ratio of coexisting upper and lower liquid layers.

The phase inversion system (a) which has relatively smaller value of V_u/V_l, namely, which is situated close to the region B, shows a strong tendency to become O-in-W emulsion by shaking of the modes (1) and (3). W-in-O emulsion which is produced only by careful shaking of the mode (2), readily turns to O-in-W emulsion by a slight up-and-down shaking. In system (b) and (c) which have a little larger value of V_u/V_l than that of the system (a), O-in-W emulsion becomes also selectively produced by the usual up-and-down shaking of the mode (3) as in the system (a), but the tendency to produce W-in-O is more remarkable in (b) and (c) than in (a). W-in-O emulsion produced in the systems (b) and (c) by shaking of the mode (2) can be inverted to O-in-W emulsion only by a strong shaking. This tendency is even more conspicuous in the system (d). In this system, both types of emulsion once established by shakings

of the modes (1) and (2) cannot be inverted each other, even by a violent shaking. In the system (d), however, there is still difference between the tendency of producing O-in-W emulsion and that of W-in-O emulsion. Emulsion of the former type is selectively produced by the usual up-and-down shaking. The tendency of producing W-in-O emulsion becomes still more marked until, at last, in system (e) and (f) which have more higher values of V_u/V_l than that of (d), the tendencies of producing both types of emulsions become equal. In such systems, two possible types of emulsions produced by shaking of the modes (1) and (2) cannot of course be inverted each other by any shaking. Moreover, usual up-and-down shaking occasionally produces both types of emulsions. Thus, in systems (e) and (f), two types of emulsions are utterly equal in their tendencies of formation on shaking. These system are, therefore, considered to be the true intermediate or boundary systems between W-in-O and O-in-W regions (A and B regions), but it is not necessary that these systems should be equally distant from both of these regions. The tendency of producing W-in-O emulsion overcomes that of O-in-W emulsion as we go further from (f) to (i) (namely, as a system approaches A region), and the emulsion of the former type is selectively

Table 5.

System	Composition in volume (c.c.)			Volume ratio		Type and stability of emulsion produced by shaking of the mode		
	Ethyl alcohol	Ethyl ether	Water	Upper layer	Lower layer	(1)	(2)	(3)
(a)	1.50	2.70	5.80	0.259	1.000	O-in-W $\Longleftarrow$ W-in-O $S_e = 8$ $S_e = 10$		O-in-W
(b)	1.50	2.80	5.70	0.293	1.000	O-in-W $\longleftarrow$ W-in-O $S_e = 8$ $S_e = 11$		O-in-W
(c)	1.50	3.00	5.50	0.348	1.000	O-in-W $\longleftarrow$ W-in-O $S_e = 8$ $S_e = 12$		O-in-W
(d)	1.50	3.10	5.40	0.372	1.000	O-in-W $\leftarrow\times\rightarrow$ W-in-O $S_e = 9$ $S_e = 14$		O-in-W
(e)	1.50	3.20	5.30	0.380	1.000	O-in-W $\leftarrow\times\rightarrow$ W-in-O $S_e = 7$ $S_e = 12$		both types
(f)	1.50	3.30	5.20	0.400	1.000	O-in-W $\leftarrow\times\rightarrow$ W-in-O $S_e = 8$ $S_e = 14$		both types
(g)	1.50	3.40	5.10	0.448	1.000	O-in-W $\leftarrow\times\rightarrow$ W-in-O $S_e = 10$ $S_e = 15$		W-in-O
(h)	1.50	3.45	5.05	0.470	1.000	O-in-W $\leftarrow\times\rightarrow$ W-in-O $S_e = 10$ $S_e = 16$		W-in-O
(i)	1.50	3.50	5.00	0.485	1.000	O-in-W $\longrightarrow$ W-in-O $S_e = 9$ $S_e = 15$		W-in-O

S_e denotes the stability of emulsion in second.
$\Longleftarrow$ inversion with ease by shaking of the mode (3).
$\longleftarrow$ inversion with difficulty.
$\leftarrow\times\rightarrow$ no inversion.

established by up-and-down shaking. The tendency of inversion from O-in-W to W-in-O also increases as the system approaches the region A. These relations can be seen in Table 5 and in Fig. 4.

In the heterogeneous binary system of ethyl ether and water, phase inversion by shaking does not occur, but some systems exhibit complex dispersion, producing both types of emulsions simultaneouly by shaking.

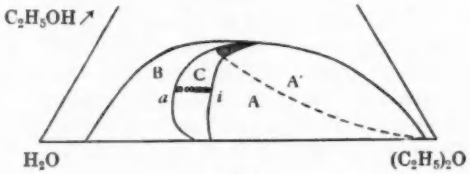


Fig. 4.

It can also be pointed out that the stability of emulsion (S_e) is not always parallel to its tendency of formation.[4] In Table 4, W-in-O emulsion is more stable than O-in-W emulsion throughout all systems of phase inversion zone, but in systems of (a), (b), (c) and (d), unstable O-in-W emulsion is selectively produced by usual up-and-down shaking. It is noted further that the tendency of producing W-in-O emulsion increases with its stability, but the increase of the tendency of producing O-in-W emulsion is not parallel to its stability.

In the heterogeneous system of EEW, there exists foam-nonfoam system, that is, the system which behaves both foamy and non foamy according to the different modes of shaking. It was indicated in the preceding paper[4] that the existence of the foam-nonfoam system is restricted in such a portion of foamy region in the heterogeneous system as it makes, at the same time, a portion of phase inversion zones. In Fig. 4, A′ surrounded by dotted line shows the foamy region of heterogeneous system of EEW, and C represents the zone of phase inversion. Hatched portion, therefore, indicates the foam-nonfoam region. The situation and nature of phase inversion system of EEW is just similar to that of AEW.[4] It foams when it is shaken by the mode (2), while it does not foam by the shaking of the mode (1).

In conclusion, the author wishes to express his hearty thanks to Prof. J. Sameshima for his valuable advice and the inspection of this paper. The expense for the experiment is defrayed from a grant given to Prof. Sameshima by Nippon Gakujutsu Shinkokwai (Japan Society for the Promotion of Scientific Research), to which the author's thanks are due.

Summary.

(1) The mutual solubility curve, tie-lines and the foam stability of homogeneous and heterogeneous system of ethyl alcohol–ethyl ether–water (EEW) were measured. The diagram was established to show the relation between the foam stability and the composition. It shows two maxima of foam stability, one of which is situated along the mutual solubility curve, and the other is on the line of ethyl alcohol–water. The former is more remarkable in its magnitude than the latter as in the system of acetic acid–ethyl ether–water (AEW). The diagram shows the third maximum of foam stability but it is uncertain.

(2) Heterogeneous system of EEW is divided into three portions referring to the type of emulsion produced by shaking, namely, W-in-O region, O-in-W region and phase inversion zone. In W-in-O or O-in-W region, a system simply produces W-in-O or O-in-W emulsion respectively, whatever the modes of shaking, while in the phase inversion zone, a system occasionally produces both types of emulsion according to the two different modes of shaking. In the phase inversion zone, the tendency to produce W-in-O emulsion gradually decreases and the tendency to produce O-in-W emulsion increases as a system changes in composition from those near W-in-O region to those near O-in-W region.

(3) Foam-nonfoam system can also be observed in this system as in AEW or acetic acid–benzene–water system. The region of its existence was determined.

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The Effect of the Silent Electrical Discharge on the Synthesis of Monochloroacetic Acid.

By Yutaka ISOMURA.

(Received May 2, 1939.)

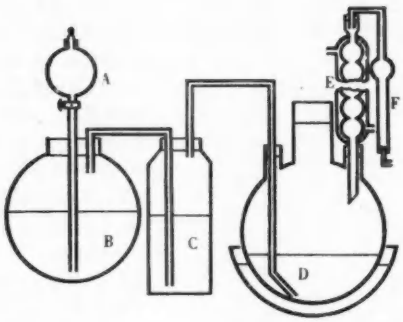
I. Red Phosphorus as Catalyser.

Monochloroacetic acid has been simply prepared with catalysers such as red phosphorus,[1] iodine,[1] sulphur,[2] etc., by bubbling vigorously gaseous chlorine into acetic acid in direct sun-light and its yield has never exceeded 60.6%.[3] In the present research, instead of direct sun-light, the silent electrical discharge was applied for the activation of chlorine and it was found that the discharge is so effective as to increase 15–100% of the best yield of monochloroacetic acid ever obtained.

Apparatus. The usual apparatus (Fig. 1) was improved as shown in Fig. 2, to increase the effect of the discharge. An induction coil is used (primary circuit: constant current of 3 A., 8 V.; secondary circuit: 0.25 mA., 14000 V.).

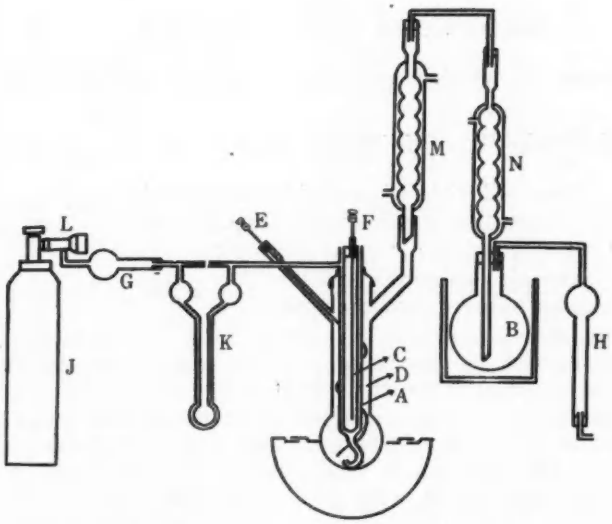
Experimental. At every run of experiments the followings have been kept the same: temperature, 100°C., 7 g. of red phosphorus, and 70 c.c. of acetic acid (99–100%), while the volume of chlorine passed

(1) H. Müller, *Ann.*, **133** (1865), 156.
(2) Anger and Behall, *Bull. s c. chim.*, [3], **2** (1889), 145.
(3) Cohen, "Practical Organic Chemistry", 106, London (1930).



A: Conc. H_2SO_4
B: $CaOCl_2$
C: Conc. H_2SO_4
D: CH_3COOH + catalyser
E: 50 cm. Liebig Condenser
F: $CaCl_2$ tube.

Fig. 1.



A: Outside electrode.
B: CH_3COCl collector. (cooled by immersing in ice water)
C: Inner electrode in dil. H_2SO_4
D: CH_3COOH + catalyser.
E: To the earth.
F: To the secondary circuit of the induction coil.
G, H: $CaCl_2$ tube.
J: Cl_2 bomb.
K: Cl_2 flowmeter.
L: Microdrive auxiliary valve.
M: 50 cm. Liebig condenser.
N: 40 cm. Liebig condenser.

Fig. 2.

into acetic acid in unit time and the duration of the reaction have been varied. The experimental results are shown in Table 1–3, and Fig. 3–8.

There is a linear relation between the pressure difference of chlorine in the flowmeter and the volume of chlorine bubbled into acetic acid per minute, as in shown in Fig. 3.

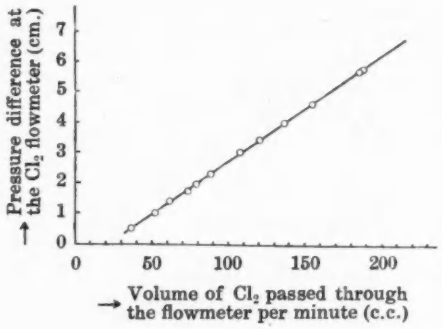


Fig. 3.

Careful observations of the reaction permit attention to the following points as to the mechanism of the reaction.

(1) An abundant quantity of acetyl chloride is formed in the reaction.

(2) The behaviour of phosphorus as catalyser is not a simple carrier of chlorine and it is often dissolved completely into the reacting system. By the quantitative analysis on the residue of the distillation, the following substance are found in the extracts by water.

$$CH_3COOH : HCl : H_3PO_4 = 1.3 : 1 : 37.5$$

(3) The equation which was formerly believed to explain the reaction being

$$CH_3COOH + Cl_2 = CH_2ClCOOH + HCl \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(A)},$$

the values $\dfrac{\text{Observed yield of monochloroacetic acid}}{\text{Theoretical yield by the equation (A)}} \times 100$ and

$\dfrac{\text{Volume of chlorine calculated from the yield of monochloroacetic acid by the equation (A)}}{\text{Total chlorine bubbled into the system}} \times 100$ (for example, the yield of monochloroacetic acid by passing 222 c.c. of chlorine per minute for four hours with the discharge), are too small to explain the completion of the reaction as is shown in Table 3.

To clear up these points and to modify the former views about the mechanisms of the reaction, the following new equation is proposed by the author. The equation is made up in a simple form from many individual processes which were previously investigated by Brückner[4]. That is

$$2P + 6CH_3COOH + 9Cl_2 = 2CH_3COCl + 6HCl + 4CH_2ClCOOH + 2POCl_3 \quad \ldots\ldots \text{(E)}.$$

Judging from the values calculated by the equation (E) in the Table 1–3 and in Fig. 4–8, it will be found that the above mentioned points are cleared up by this equation. Though it may not be of an exclusive nature, it will at least indicate the principal mechanism of the reaction.

(4) Brückner, *Z. angew. Chem.*, **50** (1928), 226.

Table 1. Acetic acid : 70 c.c. ; Duration of reaction : 2 hours ; Catalyser : red phosphorus 7 g.

No. of experiments	1	2	3	4	5	6	7	8	9	10	11	12
Preess. diff. at the Cl_2 flowmeter (cm.)	3	3	4	4	4.5	5	5	6	6	7	7	7
Duration of electric discharge (hours)	—	2	—	2	2	—	2	—	2	—	2	2
Total vol. of Cl_2 passed at 0°, 1 atm. (litres)	12.2	12.2	15.2	15.2	16.85	18.55	18.55	21.71	22.63	25.13	25.13	25.15
Total yield of $CH_2ClCOOH$ (g.)	4	6	8	11	14	9	15	11	19	14	26	22
$\frac{CH_2ClCOOH \text{ produced}}{CH_3COOH \text{ taken}} \times 100$	5.55	8.17	10.85	15.0	19.1	12.2	20.5	15.0	27.2	19.1	35.5	29.9
$\frac{\text{Observed yield}}{\text{Theoretical yield by (A)}} \times 100$	3.44	5.15	6.88	9.5	12.05	7.75	12.9	9.5	17.2	12.05	22.3	18.93
$\frac{\text{Observed yield}}{\text{Theoretical yield by (E)}} \times 100$	5.18	7.78	10.35	14.18	18.2	11.62	19.5	14.18	26.0	18.2	33.7	28.5
Yield per litre of Cl_2 (g.)	0.33	0.49	0.53	0.73	0.85	0.48	0.82	0.51	0.88	0.56	1.03	0.87
$\frac{\text{Vol. of } Cl_2 \text{ calc. for (A)}}{\text{Vol. of } Cl_2 \text{ passed}} \times 100$	7.78	11.66	12.2	17.14	19.7	14.46	19.17	15.3	20.82	13.2	24.52	20.74
$\frac{\text{Vol. of } Cl_2 \text{ calc. for (E)}}{\text{Vol. of } Cl_2 \text{ passed}} \times 100$	17.48	26.2	28.06	38.55	44.32	25.85	43.1	34.37	46.83	29.7	55.15	46.6
CH_3COCl in the collector (g.)	2	2	2	2	2	2	3	3	3	3	4	4

Table 2. Acetic acid : 70 c.c. ; Duration of reaction : 3 hours ; Catalyser : red phosphorus 7 g.

No. of experiments	1	2	3	4	5	6	7	8	9	10	11	12	13
Press. diff. at the Cl_2 flowmeter (cm.)	2	2	3	3	4	4	5	5	6	6	6	7	7
Duration of electric discharge (hours)	—	3	—	3	—	3	—	3	—	3	3	—	3
Total vol. of Cl_2 passed at 0°, 1 atm. (litres)	13.52	13.52	18.34	18.56	22.95	22.65	27.93	28.38	32 37	32.91	32.91	37.10	37.8
Total yield of $CH_2ClCOOH$ (g.)	10	17	18	28	25	35	34	45	40	48	49	45	54
$\frac{CH_2ClCOOH \text{ produced}}{CH_3COOH \text{ taken}} \times 100$	13.6	23.2	24.5	38.2	34.0	47.7	46.0	61.2	53.6	65.3	66.8	61.2	73.5
$\frac{\text{Observed yield}}{\text{Theoretical yield by (A)}} \times 100$	8.6	14.7	15.4	24.1	21.5	30.1	29.2	38.7	34.4	41.3	42.1	38.7	46.6
$\frac{\text{Observed yield}}{\text{Theoretical yield by (E)}} \times 100$	12.95	22.1	23.3	36.3	32.3	45.5	44.0	58.5	52.0	62.2	63.5	58.5	70.0
Yield per litre of Cl_2 (g.)	0.74	1.25	0.99	1.51	1.09	1.55	1.22	1.58	1.24	1.46	1.49	1.21	1.43
$\frac{\text{Vol. of } Cl_2 \text{ calc. for (A)}}{\text{Vol. of } Cl_2 \text{ passed}} \times 100$	17.53	29.81	23.10	35.8	25.8	36.6	23.9	37.6	29.3	34.52	35.3	28.8	33.8
$\frac{\text{Vol. of } Cl_2 \text{ calc. for (E)}}{\text{Vol. of } Cl_2 \text{ passed}} \times 100$	39.3	67.06	52.35	80.46	57.83	82.4	64.9	84.5	65.9	77.8	79.4	64.7	76.2
CH_3COCl in the collector (g.)	3	3	5	?	8	8	10	8	10	10	6	4	5

Table 3. Acetic acid : 70 c.c. ; Duration of reaction : 4 hours ; Catalyser : red phosphorus 7 g.

Table 3. Acetic acid: 70 c.c.; Duration of reaction: 4 hours; Catalyser: red phosphorus 7 g.

No. of experiments	1	2	3	4	5	6	7	8	9	10	11
Press. diff. at the Cl_2 flowmeter (cm.)	1.4	1.4	2	2	2	2	2.75	2.75	2.75	2.75	4
Duration of electric discharge (hours)	—	4	—	—	4	4	—	—	4	4	—
Total vol. of Cl_2 passed at 0°, 1 atm. (litres)	13.97	14.01	17.47	17.92	17.83	17.93	22.31	21.96	22.30	22.14	30.59
Total yield of $CH_2ClCOOH$ (g.)	5	12	9	12.2	19.8	18	15	17	32.3	34.3	30.5
$\frac{CH_2ClCOOH \text{ produced}}{CH_3COOH \text{ taken}} \times 100$	6.8	16.3	12.2	16.6	26.9	24.5	20.3	23.0	43.7	46.4	41.5
$\frac{\text{Observed yield}}{\text{Theoretical yield by (A)}} \times 100$	4.3	10.3	7.7	10.5	17.0	15 5	12.9	14 6	27.8	29.5	26.2
$\frac{\text{Observed yield}}{\text{Theoretical yield by (E)}} \times 100$	6.5	15.6	12.2	16.1	25.7	23.3	19.4	22.2	42.0	44.0	39.5
Yield per litre of Cl_2 (g.)	0.36	0.86	0.52	0.67	1.11	1 0	0.67	0.78	1.44	1.56	0.99
$\frac{\text{Vol. of } Cl_2 \text{ calc. for (A)}}{\text{Vol. of } Cl_2 \text{ passed}} \times 100$	8.48	20.3	12.2	16.1	26.3	26.5	15.9	18.4	34.4	36.8	23.6
$\frac{\text{Vol. of } Cl_2 \text{ calc. for (E)}}{\text{Vol. of } Cl_2 \text{ passed}} \times 100$	19.1	45.7	27.5	36.3	59.2	53.5	35.9	41.3	77.3	82.6	53.2
CH_3COCl in the collector (g.)	3	5	5	8	8	8	8	8	8	10	15

No. of experiments	12	13	14	15	16	17	18	19	20	21
Press. diff. at the Cl_2 flowmeter (cm.)	4	4	4	5	5	6	6	6	7	7
Duration of electric discharge (hours)	—	4	4	—	4	—	4	4	—	4
Total vol. of Cl_2 passed at 0°, 1 atm. (litres)	30.66	30.37	30.70	37.74	36.78	43.78	43.18	43.2	50.86	49.73
Total yield of $CH_2ClCOOH$ (g)	29	47	46	40	62	49	70	68	54	73
$\frac{CH_2ClCOOH \text{ produced}}{CH_3COOH \text{ taken}} \times 100$	39.4	63.9	62.7	53.1	87.0	67.0	95.2	92.5	73.7	99.3
$\frac{\text{Observed yield}}{\text{Theoretical yield by (A)}} \times 100$	25.0	40.4	39.5	34.4	56.0	42.3	60.2	58.5	46 5	62.8
$\frac{\text{Observed yield}}{\text{Theoretical yield by (E)}} \times 100$	37.6	61.0	59.6	51.8	80.5	63.5	91.0	88.0	70.0	94.5
Yield per litre of Cl_2 (g.)	0.94	1.52	1.50	1.06	1.68	1.12	1.62	1.57	1.06	1.47
$\frac{\text{Vol. of } Cl_2 \text{ calc. for (A)}}{\text{Vol. of } Cl_2 \text{ passed}} \times 100$	22.4	36.7	35.5	25.1	40.0	26.5	38.4	37.4	25.5	34.8
$\frac{\text{Vol. of } Cl_2 \text{ calc. for (E)}}{\text{Vol. of } Cl_2 \text{ passed}} \times 100$	50 5	82.5	79.9	56.5	89.9	59.6	86.5	83.9	56.6	78 3
CH_3COCl in the collector (g.)	15	3	5	10	10	15	10	15	15	15

In Fig. 4–11

- ⊙ 2 hours' reaction with discharge
- ○ 2 hours' reaction without discharge
- ● 3 hours' reaction with discharge
- ◑ 3 hours' reaction without discharge
- ⊗ 4 hours' reaction with discharge
- ◒ 4 hours' reaction without discharge

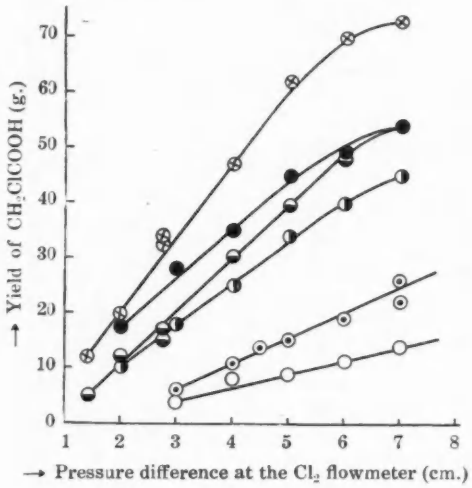


Fig. 4.

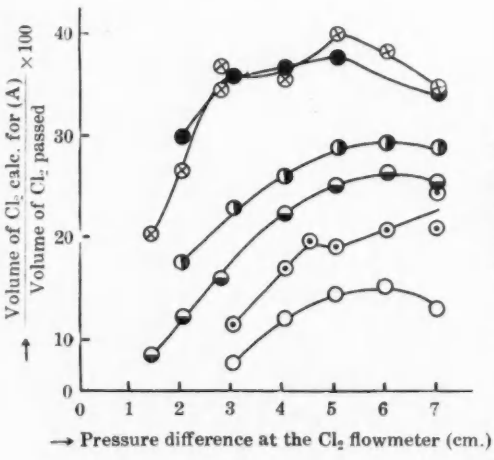


Fig. 5.

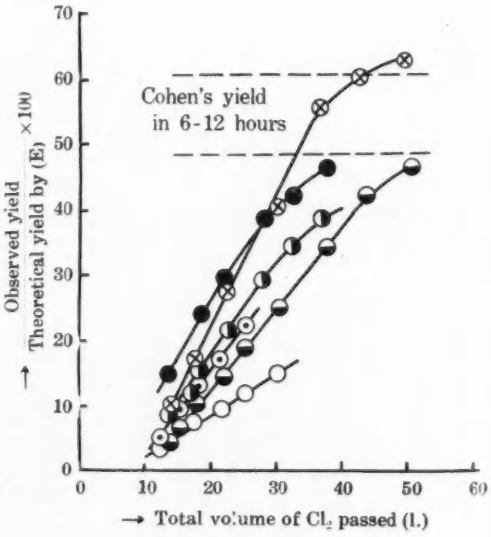


Fig. 6.

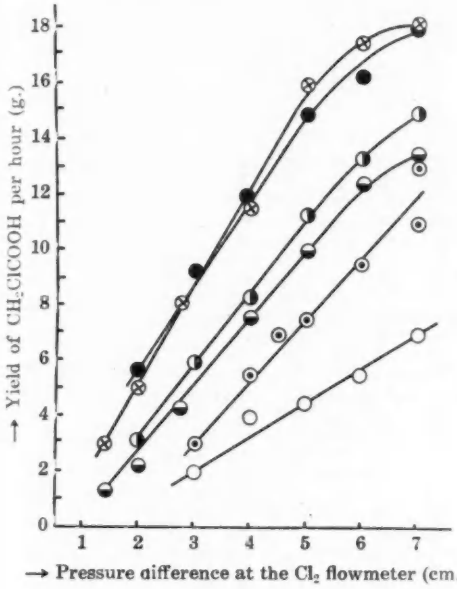


Fig. 7.

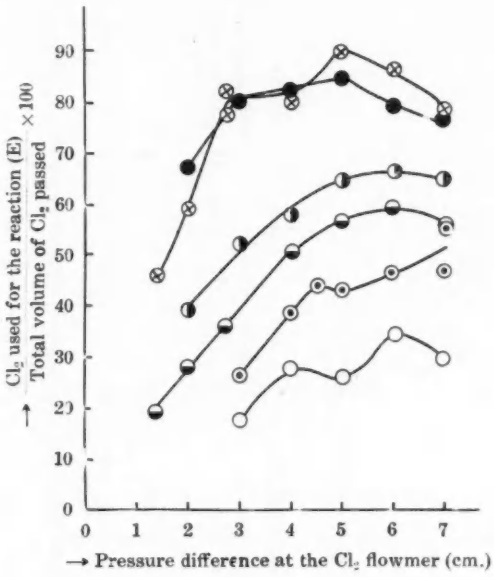


Fig. 8.

II. Iodine, Red Phosphorus, and Phosphorus Pentachloride as Catalyser.

Brückner[4] reported that he obtained 66% of monochloroacetic acid in four hours by using 1 g. I_2 + 2 g. P_4 + 2 g. PCl_5 as catalyser and bubbling 245 c.c. of chlorine per minute through acetic acid. This result was so amazing that even now this catalyser maintains its industrial application.

The experiments were carried out by the present author with the same catalyser in much the same way as was previously mentioned and the same results as those of Brückner were obtained. However, by using 1 g. of iodine for 70 c.c. of acetic acid, a great deal of difficulties were found to eliminate iodine vapour from every fraction of the distillation. The amount of iodine was then diminished from 1 g. to 0.2 or 0.1 g. so far as the yield of monochloroacetic acid was not affected. With the modified catalyser, that is 0.1–0.2 g. I_2 + 2 g. P_4 + 2 g. PCl_5, the experiments were carried out to see the effect of the silent electrical discharge on the synthesis of monochloroacetic acid. As the result, the yield of monochloroacetic acid was increased in a great extent and the elimination of iodine from the product was satisfactory by carrying out the distillation at 180–190°C.[5]

(5) Even if 0.1 or 0.2 g. of iodine is used for 70 c.c. of acetic acid, the distillates between 180 and 190°C. have sometimes pinc tint. It is found that 0.5–1% of active charcoal is effective enough to decolourize such a small quantity of iodine in monochloroacetic acid. Iodine is completely adsorped by charcoal at the temperature between 180 and 190°C.

Table 4. Acetic acid: 70 c.c.; Duration of reaction: 2 hours.

Catalyser	0.1 g. I_2 + 2 g. P_4 (red) + 2 g. PCl_5												1 g. I_2+2 g. P_4+2 g. PCl_5		
No. of experiments	1	2	3	4	5	6	7	8	9	10	11	12	13	14	Brückner (Acetic acid: 100 c.c.)
Press. diff. at the Cl_2 flowmeter (cm.)	3	3	3	4	4	5	5	6	6	6	7	7	5	6	7.9
Duration of electric discharge (hours)	—	2	2	—	2	—	2	—	2	2	—	2	—	2	—
Total vol. of Cl_2 passed at 0°, 1 atm. (litres)	12.0	11.91	11.9	15.18	14.92	17.28	17.28	21.28	21 3	21.49	24.66	25.12	17.77	21.28	29 4
Total yield of $CH_2ClCOOH$ (g.)	22	25	25	30	34	38	43	42	47	51	53	60	40	49	64
$\frac{CH_2ClCOOH \text{ produced}}{CH_3COOH \text{ taken}} \times 100$	30.0	34 0	34.0	40.8	46.3	51.8	58.5	57.2	64.0	69.5	72.3	81.8	54.5	66.8	64
$\frac{\text{Observed yield}}{\text{Theoretical yield by (A)}} \times 100$	18.8	21.5	21.5	23.8	29.2	32.7	37.0	36 1	40 5	43.8	45.5	51.2	34.4	42.2	40.6
Yield per hour (g.)	11	12.5	12.5	15	17	19	21.5	21	23 5	25.5	26.5	30	20	24.5	32.0
Yield per litre of Cl_2 (g.)	1.83	2.09	2.09	1.97	2.28	2.19	2.48	1.97	2.20	2.37	2,15	2.39	2.25	2.30	2.17
$\frac{\text{Vol. of } Cl_2 \text{ calc. for (A)}}{\text{Vol. of } Cl_2 \text{ passed}} \times 100$	43.5	49.8	49.8	46.8	54.0	52.1	59.0	46.8	51.2	56.3	51.0	56.5	52.1	54.6	51.6
CH_3COCl in the collector (g.)	2	2	2	2	2	2	2	2	2	2	2	2	2	2	?

Table 5. Acetic acid: 70 c.c.; Duration of reaction: 3 hours; Catalyser: 0.1 g. iodine + 2 g. red phosphorus + 2 g. phosphorus pentachloride.

No. of experiments	1	2	3	4	5	6	7	8	9	10	11	12
Press. diff. at the Cl_2 flowmeter (cm.)	3	3	3	4	4	5	5	6	6	6	7	7
Duration of electric discharge (hours)	—	—	3	—	3	—	3	—	3	3	—	3
Total vol. of Cl_2 passed at 0°, 1 atm. (litres)	18.25	18.28	18.25	22.96	22.81	27.88	27.88	33.32	33.13	33.13	37.87	38.34
Total yield of $CH_2ClCOOH$ (g.)	44	46	49	59	62	69	77	80	85	84	80	92
$\frac{CH_2ClCOOH \text{ produced}}{CH_3COOH \text{ taken}} \times 100$	60.0	62.8	66.8	80.5	84.5	94.0	104 6	108.5	115.6	114.0	108.5	125.0
$\frac{\text{Observed yield}}{\text{Theoretical yield by (A)}} \times 100$	37.8	39.7	42 2	50.8	53.3	59.3	66.2	68.8	73.2	72.2	68.8	79.2
Yield per hour (g.)	14.7	15.3	16.3	19.7	20.7	23.0	25.7	26.7	28.3	28.0	26.7	30.7
Yield per litre of Cl_2 (g.)	2.41	2.51	2.68	2.58	2.72	2 47	2.76	2.40	2.56	2.53	2.11	2.40
$\frac{\text{Vol. of } Cl_2 \text{ calc. for (A)}}{\text{Vol. of } Cl_2 \text{ passed}} \times 100$	57.2	59.6	63.6	60.9	64.4	58.7	65.5	56.9	60.8	60.1	50.1	56.9
CH_3COCl in the collector (g.)	2	2	2	2	2	2	2	2	2	2	2	3

Table 6. Acetic acid: 70 c.c.; Duration of reaction: 4 hours; Catalyser: 0.1 g. iodine + 2 g. red phosphorus + 2 g. phosphorus pentachloride.

No. of experiments	1	2	3	4	5	6	Brückner (Acetic acid: 100 c.c. $1g.\ I_2+2g.\ P_4+2g.\ PCl_5$)
Press. diff. at the Cl_2 flowmeter (cm.)	3	3	4	4	5	5	7.9
Duration of electric discharge (hours)	—	4	—	4	—	4	—
Total vol. of Cl_2 passed at 0°, 1 atm. (litres)	24.43	24.43	30.46	30.46	36.94	36.91	58.8
Total yield of $CH_2ClCOOH$ (g.)	68	74	84	88	90	93	104
$\frac{CH_2ClCOOH\ produced}{CH_3COOH\ taken}\times 100$	92.6	100.6	114	119 5	122.5	126.5	104
$\frac{Observed\ yield}{Theoretical\ yield\ by\ (A)}\times 100$	58.5	63.5	72.0	75.5	77.4	80.0	66.0
Yield per hour (g.)	17	18.5	21	22	22.5	23.3	19.1
Yield per litre of Cl_2 (g.)	2.78	3.03	2.76	2.89	2.43	2.52	1.77
$\frac{Vol.\ of\ Cl_2\ calc.\ for\ (A)}{Vol.\ of\ Cl_2\ passed}\times 100$	66.0	71.8	65.4	68.5	57.7	59.7	41.9
CH_3COCl in the collector (g.)	3	3	3	3	3	3	?

$\rightarrow \frac{Cl_2\ used\ for\ the\ reaction}{Total\ volume\ of\ Cl_2\ passed}\times 100$

From the experiments the followings can be perceived.

(1) Iodine is dissolved in acetic acid as ICl or ICl_3 and thus serves for the equal distribution of chlorine in the system. By the thermal decomposition in the distillation, iodine is again set free from ICl or ICl_3 and is mixed in every distillate.

(2) The yield of acetyl chloride is far less than that of the previous experiment (only 2.5 g in four hours).

(3) Phosphorus pentachloride serves to produce acetyl chloride in adequate amount and velocity.

(4) Sometimes a part of phosphorus is dissolved, but in the majority of the experiments it maintains its initial amount, and the yield of monochloroacetic acid never fluctuates as it does otherwise by the diminution of the amount of phosphorus.

From the above mentioned facts we may conclude that the main mechanism of the reaction is expressed by the equation (A), and that the added substances take rôle of the catalyser.

Not only from the above mentioned facts, but also from the values calculated by the equation (A) as is shown in Table 4–6, and Fig. 9–11, the equation seems to be correct.

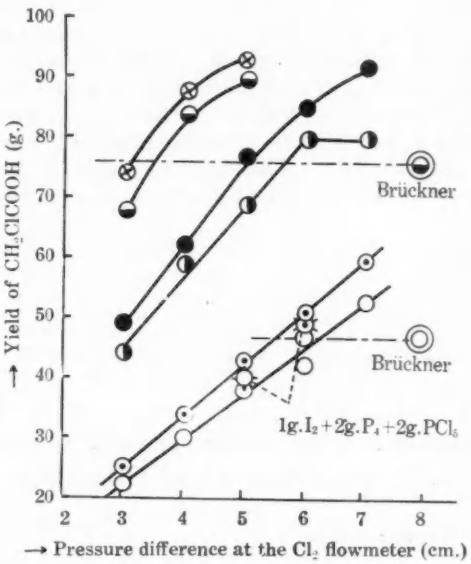


Fig 9.

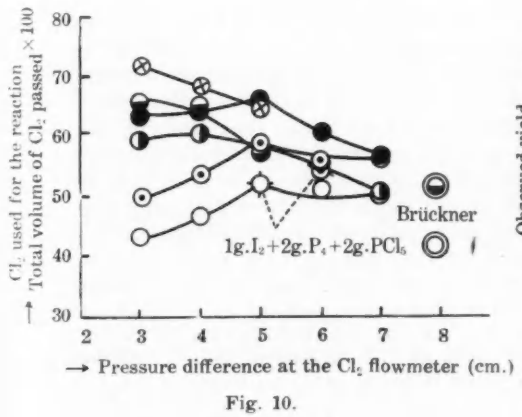

Cl_2 used for the reaction / Total volume of Cl_2 passed ×100
Brückner
1g.I_2+2g.P_4+2g.PCl_5
→ Pressure difference at the Cl_2 flowmeter (cm.)

Fig. 10.

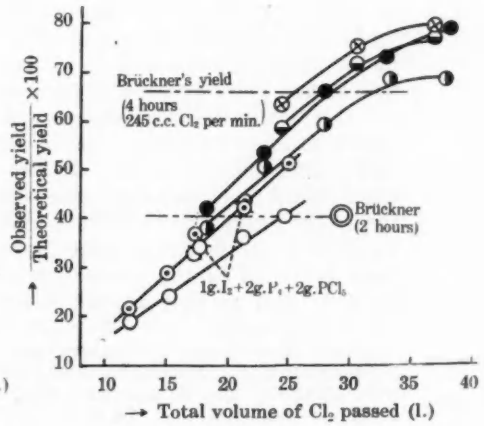


Fig. 11.

Summary.

(1) Silent electrical discharge is very effective to produce monochloroacetic acid from acetic acid and chlorine by using red phosphorus as catalyser, and it increases 15–100% of the yield of monochloroacetic acid compared with the formerly obtained results. The yield of 62.8% in four hours running is one of the best record that is attained in the experiment using red phosphorus (10%) as catalyser. A new equation (E) is proposed to clear up several questions involved in the formerly believed equation (A).

(2) The reaction between acetic acid and chlorine was carried out under the influence of the silent electrical discharge, using iodine, red phosphorus, and phosphorus pentachloride as catalyser. The reaction is expressed by the equation (A). The yields of 79.2% in the reaction for three hours discharge and 80.0%, for four hours discharge, are far better than the yield of 66% reported by Brückner. This is chiefly due to the effect of the new modified catalyser and of the silent electrical discharge.

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Studies on the Oiliness of Liquids. VII. Measurements of the Static Friction Coefficients of Esters, Ketones and Glycerine.

By Toshizo ISEMURA.

(Received May 23, 1939.)

The measurements of the static friction of glass surfaces, when various organic liquids are present as lubricant, have already been reported in the previous papers.[1] The liquids tested contain polar compounds as well as non-polar ones. The former consists, mostly, of alcohol and normal acids, which have the polar group at one end of their molecules. It is interesting to know whether the shape of the molecule has the effect on the lubricating activity or not. In the present experiments, therefore, esters and ketones have been tested as lubricating liquids. These compounds have the polar group at the middle part of the molecule. Glycerine was also tested, which has three polar groups in a relatively small molecule. We have reported in the preceding papers, that the friction coefficients of water[2] and methyl alcohol[3] are 0.75 and 0.62 respectively. These

(1) J. Sameshima, M. Kidokoro and H. Akamatu, this Bulletin, **11** (1936), 659; H. Akamatu and J. Sameshima, *ibid.*, **11** (1936), 791; J. Sameshima and Y. Tsubuku, *ibid.*, **12** (1937), 127; H. Akamatu, *ibid.*, **13** (1938), 127.

(2) H. Akamatu, *ibid.*, **13** (1938), 131.

(3) J. Sameshima, M. Kidokoro and H. Akamatu, *ibid.*, **11** (1936), 663.

data have been revised and found that they are somewhat too low. The results will be described in the following lines.

The experiment was pursued by the balance method. The friction surfaces consisted of a flat glass and a glass with a spherical surface. They were cleaned sufficiently prior to each experiment by the same method as described in the former paper. The purest samples available were used in the experiments. All esters and ketones were sufficiently dried with quick lime or anhydrous potassium carbonate and then distilled before the experiment. Glycerine was distilled six times in vacuum to expel the last trace of water contained in it. The measurements were conducted at room temperature without any special adjustment of temperature because the coefficient of friction is not seriously affected by the change of temperature. The results obtained are summarised in Table 1. Fig. 1 shows the relations between the friction coefficient and the number of carbon atoms in the molecule of the substance.

Table 1.

Lubricant	W	F	μ
Methyl acetate	21.55	18.52	0.86
	21.55	18.52	0.86
	23.85	20.90	0 88
	23.85	21.70	0.91
	27.00	22.88	0.85
	27.00	22.18	0.82
	29.30	26.95	0.92
			0.87
Ethyl acetate	21.55	17.50	0.81
	25.40	21.12	0.83
	27.00	21.60	0.80
	29.30	23.70	0.81
	29.40	24.18	0.82
			0.81
n-Propyl acetate	14.50	12.00	0 83
	17.00	13.18	0.78
	19 30	15.55	0.81
	19.30	15.15	0.79
	27.00	21.30	0.79
	29.30	24.25	0.83
			0.81
n-Butyl acetate	19.40	15.43	0.80
	23.85	19.08	0.80
	27.00	20.64	0.77
	29 30	22.40	0.77
	31.70	23.99	0.76
	35.40	26.50	0.75
	37.70	31.40	0.83
			0.78
n-Amyl acetate	21.55	15.60	0.73
	23.55	17.30	0.74
	23.85	17.70	0.74
	27.70	19.48	0.72
	29.30	22.38	0.76
	29.30	21.80	0.74
	37.70	27.88	0.75
			0.74
n-Octyl acetate	21.55	15.54	0.72
	23.85	17.05	0.72
	27.00	19.33	0.72
	29.30	21.64	0.74
	35.40	25.78	0.72
	37.70	28.90	0.77
			0.73
Ethyl propionate	14.10	11.90	0.85
	15.70	13.20	0.84
	19.30	15.05	0.78
	23.35	17.70	0.76
	29.30	23.10	0.79
	30.05	23.80	0.79
	33.35	26.10	0.79
			0.80
Ethyl butylate	15.00	12.20	0.81
	16.60	13.10	0.79
	23.85	19.50	0.82
	27.00	21.60	0 80
	27.90	22.02	0.79
	29.30	23.10	0.79
	31.55	24.98	0.79
			0 80
Acetone	14.35	12.54	0.88
	17.30	14.80	0.86
	18.35	14.89	0.81
	21.05	18.25	0.87
	27.02	23.20	0.86
			0.86

Table 1.—(*Concluded*)

Lubricant	*W*	*F*	μ	Lubricant	*W*	*F*	μ
Methyl ethyl ketone	21.30	17.65	0.83	Glycerine	25.70	21.43	0.84
	21.30	17.35	0.81		48.40	42.30	0.88
	24.30	19.20	0.79				0.86
	26.30	22 40	0.85				
	26.30	21.70	0.83				
	29.30	25.00	0 85				
			0.83	Water	16.05	14.35	0.89
					19.45	17.83	0.92
					20.75	19.20	0.93
Diethyl ketone	17.00	13.85	0.82		20.80	19.50	0.94
	19.30	15.95	0.83		22.70	19.65	0.87
	19.30	15.96	0.83		24.50	21.30	0.87
	23.35	20.00	0.86		26.15	23.60	0.90
	27.00	23.12	0.86				0.90
	29.30	25.95	0.81				
			0.84				
Acetophenone	19.30	13.90	0.72	Methyl alcohol	17.10	13.79	0.81
	27.00	19.15	0.71		20.30	16.45	0.81
	29.30	20.82	0.71		20.85	15.98	0.77
	29.30	22.18	0.76		21.50	15.86	0.74
	29.30	21.25	0.73		23.70	18.47	0.78
	31.05	22.40	0.72		24.15	19.45	0.81
	33.35	25.05	0.75				0.79
	33.85	24.01	0.71				
			0.73				

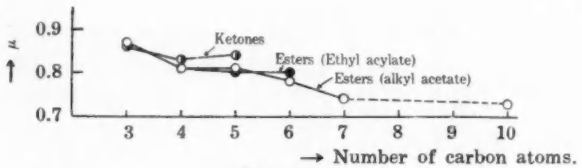

Fig. 1.

We know from Table 1, that all these substances—esters, ketones, and glycerine—give relatively high friction coefficients. So it may be concluded from these results, that substances which have the polar group at the middle part of the molecule do not serve as good lubricants. The polar molecule attaches to the friction surface with its polar group and presenting non-polar chain to the liquid interface, forming a monomolecularly orientated layer.[4] A substance serve as a better lubricant when molecules take regular arrangement on the sliding surface than they take irregular arrangement.[5] The esters and ketones have the polar group at the middle part of the molecule, with which they may anchor on the surface. It is recognisable from this fact that they take regular arrangement more difficultly than the molecules having polar group at the end of the molecule. This may be the reason of high friction coefficients of esters and ketones.

(4) Hardy and Doubleday, *Proc. Roy. Soc.* (London), A, **104** (1923), 25; Akamatu, this Bulletin, **13** (1938), 127.

(5) H. Akamatu and J. Sameshima, *ibid.*, **11** (1936), 793.

As already reported in the preceding papers, the lower homologous are poorer lubricants than the higher homologous in the aliphatic alcohol series.[6] The analogous fact is also observed in the ester series, although they give always higher friction coefficients than alcohols. However, the effect of chain length of alkyl group in the ester is more predominated than the effect of that of acyl group.

The high static friction coefficient of glycerine is also ascribable to its molecular structure. When glycerine is placed on the sliding surface, it attaches to the surface with its three polar groups and the molecule can hardly be inclined according to the anchoring with these groups. Moreover, no flexibility can considered of its molecule for the shortness of its chain. The fricition coefficient of water was determined to be 0.9. It is the highest friction coefficient we ever obtained on the glass surface in the pressence of lubricant. Hardy and Doubleday stated that water is neutral to the surfaces of glass or steel in that it neither lowers nor raises the friction.[7] This fact may be probably ascribable to the very short chain of the molecule.

In conclusion the author expresses his hearty thanks to Prof. J. Sameshima for his kind guidance and encouragement. The expense for the experiments has been defrayed from a grant given to Prof. Sameshima by Nippon Gakujutsu Shinkokwai (Japan Society for the Promotion of Scientific Research), to which the author's thanks are due. The author's acknowledgement is also due to Hattori Hokokwai for a grant.

Summary.

(1) The static friction coefficients have been measured when esters, ketones and glycerine are placed on the glass surface as lubricants.

(2) The friction coefficients of these liquids are very high.

(3) Some considerations have been made on the high friction coefficients of these liquids.

(4) The friction coefficients of water and methyl alcohol have been revised.

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(6) J. Sameshima, M. Kidokoro and H. Akamatu, *ibid.*, **11** (1936), 659; J. Sameshima and Y. Tsubuku, *ibid.*, **12** (1937), 127.

(7) Hardy and Doubleday, *Proc. Roy. Soc.* (London), A, **104** (1923), 34.

Geochemische Untersuchungen der Vulkane in Japan. IX. Bestimmung des Schwerwassergehaltes von den in der Nähe des Vulkans Asama befindlichen Quellwasser.*

Von Yuji SHIBATA, Kimio NOGUCHI, und Osamu KANEKO.

(Eingegangen am 24. Mai 1939.)

Über den Ursprung der aus den Kratern tätiger Vulkane oder aus den in ihren Nähen befindlichen Fumarolen ausgestossenen Wasserdämpfe sind bisher verschiedene Ansichten geäussert. Nämlich betrachtet man sie bald als juveniles Wasser, bald als vadoses Wasser oder bald als das Gemisch dieser beiden Wasserarten. Das ist ebenfalls der Fall bei der Auseinandersetzung über die Herkunft von Thermen und Pegen. Zwar einerseits vertrat Robert Bunsen die Vadoswassertheorie, als er im Jahre 1846 gelegentlich der Studienreise nach Island die Frage über die Entstehung dortiger Thermen erörtete, während andererseits Elie de Beaumont, A. Gautier u.a. behaupteten, dass das Thermalwasser im allgemeinen des magmatischen Ursprungs ist. Dagegen sind die amerikanischen Forscher, die neuerdings über die im Yellowstone Park befindlichen heissen Quellen eine interessante Untersuchung ausgeführt haben, wieder die erstere Bunsensche Theorie zu stützen geneigt.

In Bezug auf den Unterschied zwischen magmatischem (juvenilem) und vadosem Wasser wurde die folgende Ansicht von A. Gautier[1] im Jahre 1910 vorgebracht: das juvenile Wasser, seiner Meinung nach, enthält im wesentlichen Bicarbonate und Silikate von Alkali- und Schwermetalle, deren Gehalt von meteorologischen Bedingungen wenig beeinflusst wird, während das vadose Wasser überhaupt Carbonate, Sulfate und Chloride von Calcium und Magnesium auflöst, indem ihre Konzentration durch Niederschläge leicht verändert wird.

Jedoch wird die strenge Unterscheidung von diesem beiden Wasserarten im Sinne Gautiers nur schwierig durchführbar, weil das rein juvenile Wasser auf der Erdoberfläche sehr selten anzutreffen ist. Nimmt man aber an, dass die Verteilung von Wasserstoff- sowie Sauerstoff-Isotopen in juvenilem und vadosem Wasser nicht gleichartig sei, so könnte man einen sicheren Anhaltspunkt für die Erkennung dieser beiden Wasserarten gewinnen, indem man einen exakten Vergleich zwischen Dichten des zur Frage kommenden Naturwassers und des Leitungswassers, das als ein typisches vadoses Wasser betrachtet wird, anstellt.

Zahlreiche Untersuchungen von verschiedenen Forschern lehren uns tatsächlich, dass die an der Erdoberfläche weit verbreiteten vadosen Wasser (Seewasser, Flusswasser, Quellwasser, besonders Leitungswasser) immer ungefähr gleiche Dichte besitzen, während es noch keinen Beweis gibt für die Dichtegleichheit zwischen dem eben genannten Wasserart und dem von der Erdtiefe stammenden.

* Übersetzung einer Mitteilung, die in *J. Chem. Soc. Japan*, **58** (1937), 1013. auf Japanisch beschrieben.

(1) A. Gautier, *Compt. rend.*, **150** (1910), 436.

Macht man nun eine Voraussetzung, die dahin geht, dass bei der allerersten Entstehung von mineralischen Bestandteilen des heutigen Erdballs, die leichteren Isotopen der chemische Elemente mit grösserer Leichtigkeit als die schweren miteinander in Bindung eingetreten wären, so könnte man wohl daran denken, dass auch das Wasser, das seit solchen Urzeiten in der Erdtiefe verborgen bleibt, eine reichlichere Menge der leichteren Molekülen enthält als das vadose Wasser, das jetzt, wie bekannt, ein konstantes Verhältnis von leichten Molekülen zu schweren innehält.

Seit einigen Jahren sind wir mit der geochemischen Erforschung der tätigen Vulkane in Japan beschäftigt, und wir stellen z.Z. über die Gase, die Wasser, die Gesteine, die Asche u.s.w. vom Vulkan Asama, der sich seit 1935 im Zustande von lebhafter Aktivität befindet, vielseitige Untersuchungen an. Dabei haben wir auch die vergleichenden Dichtemessungen der verschiedenen Naturwasser, die hier und da in der Umgegend vom Vulkan Asama sprudeln, und des Leitungswassers von der Stadt Tokyo ausgeführt. Wie es unten näher beschrieben wird, wird es bestätigt, dass die in Frage kommenden Naturwasser meistens einige γ leichter sind als das Leitungswasser. Diese Resultate scheinen gewissermassen für unsere oben erwähnte Voraussetzung zu sprechen, aber wir wollen noch kein bestimmtes aussagen, bevor unsere weitere, mit zahlreichen Materialien fortzuführende Untersuchungen zum Abschluss kommen.

Beschreibung der Versuche. 1. *Messungsapparate.* Im wesentlichen haben wir für die Dichtemessung der Naturwasser die von M. Koizumi[2] ausgearbeitete Schwimmermethode angewandt, die aber von uns in einigen Punkten etwas verbessert würde. Der Thermostat besteht aus einer Doppelwanne, deren äussere durch das im Kochsalz-Eis-Kältegemisch zirkulierende Wasser gekühlt ist. Die Temperatur der inneren Wanne ist somit bei etwa 8° innerhalb $\pm$ 0.002° konstant gehalten; dies entspricht einem Dichteunterschiede von 0.1 γ. Der Schwimmer ist aus Quarz hergestellt, und sein Unterteil ist spindelförmig gemacht, so dass er im Probegefäss auf und ab ganz glatt bewegen kann. Die Kapazität des Probegefässes aus Pyrexglas beträgt 5 ccm.

2. *Reinigung des Probewassers.* Da die Naturwasser aus der vulkanischen Gegend im allgemeinen etwas sauer reagieren, so wird das Probewasser zuerst mit Natriumperoxyd neutralisiert und nötigenfalls filtriert. Dann wird es mit kleiner Menge von Natriumperoxyd und Kaliumpermanganat versetzt, unter Rückfluss gekocht und schliesslich vorsichtig destilliert.

Um die durch Fraktionieren verursachte Isotopentrennung zu vermeiden, wurden immer je 5 ccm. Wasser am Anfang und am Ende von jeder Destillation weggeschaffen. Das so vorläufig gereinigte Wasser wurde noch weiteren Destillationen unterworfen. Die Vorrichtung für dieses letztere Reinigungsverfahren besteht, wie in Abb. 1 gezeigt, aus drei Destillierkolben aus Pyrexglas, die von oben nach unten stufenweise angeordnet und mit Kühlern verbunden sind. Die Apparatur wurde vorher gut gewaschen und getrocknet, wobei man das ganze System hindurch die getrocknete und kohlensäurefreie Luft durchströmen lässt. Bei der

(2) M. Koizumi, *J. Chem. Soc. Japan*, **56** (1935), 811.

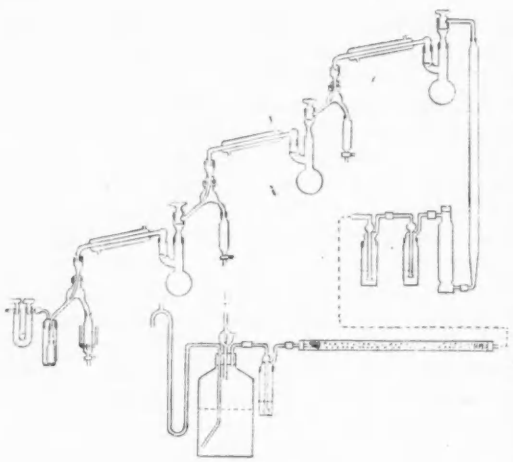

Abb. 1.

Destillation trägt man eine kleine Menge von P_2O_5 in den ersten Kolben und wenig Bariumhydroxyd in den zweiten Kolben ein. Die allerletzte Destillation aus dem dritten Kolben wird ohne Zusatz sehr vorsichtig ausgeführt. Die Reinheit des so behandelten Wassers wurde durch die Messung der Leitfähigkeit geprüft, deren Werte $0.6 \sim 2 \times 10^{-6}$ rezip. Ohm betrugen.

3. *Standardwasser.* Der Erfolg der Dichteunterschiedsmessung nach der Schwimmermethode beruht überhaupt auf der strengen Unveränderlichkeit des Standardwassers. Deshalb haben wir am 15. April 1935, eine grosse Menge städtischen Leitungswassers in einer gut verschliessbaren Flasche aufbewahrt. Die Reinigung desselben wurde genau gleich wie beim Probewasser vorgenommen.

4. *Gleichgewichtstemperatur.* Die Bestimmung der Gleichgewichtstemperatur wurde nach der Briscoeschen Methode[3] ausgeführt; es handelt sich nämlich um die Tatsache, dass innerhalb der engen Temperaturgrenze von 0.1° die Geschwindigkeit von auf- oder abwärts bewegendem Schwimmer mit der Differenz zwischen der betreffenden Temperatur und der Gleichgewichtstemperatur in streng linearem Verhältnis steht. Demnach wird die Gleichgewichtstemperatur nach graphischer Methode verhältnismässig einfach ermittelt, wenn man die Geschwindigkeit des bewegenden Schwimmers bei einigen bestimmten Temperaturen genau

Abb. 2.

(3) H. V. A. Briscoe, *J. Chem. Soc.* **1934,** 1207.

↑ Dichteunterschied (γ)
↑ Dichteunterschied (γ)

notiert. Die Fehlergrenze beträgt dabei etwa $\pm 0.5\,\gamma$ in bezug auf Dichteunterschied.

Ergebnisse der Dichtemessungen. Auf der vereinfachten Karte vom Vulkan Asama (Abb. 2) wurden die Örtlichkeiten der Probenahme mit den Ziffern angezeigt, die sich auch auf die Tabelle beziehen. Obgleich einige der gewonnenen Werte für den Dichteunterschied innerhalb der Fehlergrenze liegen, ist es doch merkwürdig, dass es kein Quell-, Thermen- und Mineralwasser gibt, die schwerer sind als das Leitungswasser von der Stadt Tokyo.

Um weiter zu sehen, ob man imstande wäre, bestimmte Beziehungen zwischen den Dichten und den anderen Eigenschaften des Naturwassers ausfindig zu machen, haben wir sie graphisch dargestellt, indem der Dichteunterschied ($D_{\text{Nat.}}-D_{\text{Leit.}}$) als Ordinaten und die anderen Werte, wie Wassertemperatur, Menge der Abdampfrückstände, pH-Wert, Gehalt an gewissen Ionen u.s.w., als Abszissen aufgetragen sind. Kurze Besprechungen über die erhaltenen Kurven werden folgendermassen gegeben:

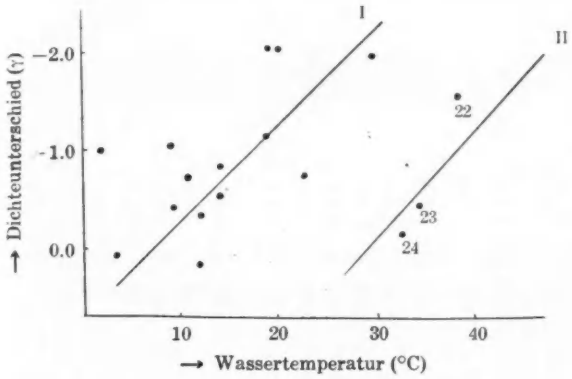

Abb. 3.

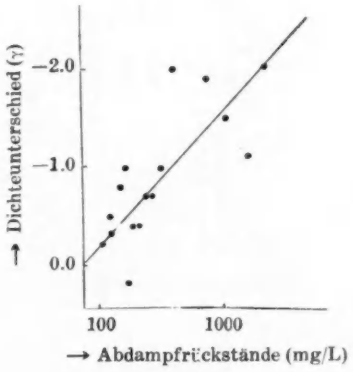

Abb. 4.

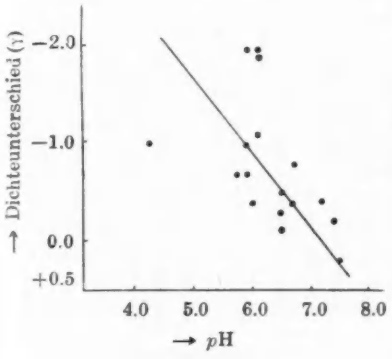

Abb. 5.

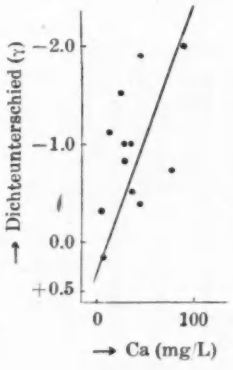

Abb. 6.

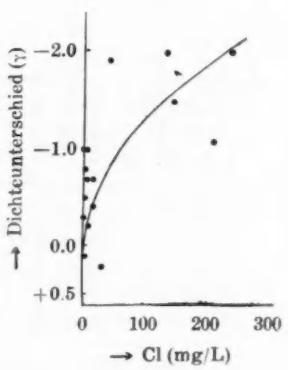

Abb. 7.

Nr.	Herkunft der Wasserprobe	Datum	Dichteunterschied ($D_{Nat.} - D_{Leit.}$)	Höhe von Meeresspiegel m	Wassertemperatur °C	pH	Abdampfrückstände mg/L	Fe mg/L	Ca mg/L	Cl mg/L	SiO_3 mg/L
25	Wasserfall von Sengataki	14. Juni 1935	+0.2	1180	11.6	7.5	315	0.26	10.1	31.6	75
5_1	Mineralwasser aus Jigokudani	14. Oktober 1934	+0.1	1920	3.2	2.66	1692	67.7	103.	3.9	37
24	Mineralwasser aus Sengataki	14. Juni 1935	−0.1	1150	32.0	6.5	3217	0.64	407.	731.	67
14	Flusswasser von Tikumagawa	12. Juni 1935	−0.2	600	—	7.4	140	0.42	—	8.7	91
16	Sprudel vom Sinrakuji-Teich	12. Juni 1935	−0.3	910	11.8	6.5	185	0.24	7.9	3.5	67
23	Thermalwasser (II) von der Hosino-Therme	14. Juni 1935	−0.4	1000	33.8	7.2	1230	0.20	47.8	176.3	63
21	Bohrungsquellwasser von Yamaya (Oiwake)	22. August 1935	−0.4	990	—	6.0	408	3.31	—	16.3	62
34	Bohrungsquellwasser von Katayama (Oiwake)	10. Dezember 1935	−0.4	990	9.0	6.7	376	3.79	—	15.7	43
17	Mineralwasser von Oyati	12. Juni 1935	−0.5	870	13.9	6.5	183	0.32	38.5	4.1	68
18	Quellwasser vom Fluss Nigorigawa	26. April 1935	−0.7	1490	10.5	5.74	473	77.3	78.3	12.5	74
29	Mineralwasser von Osasa	15. Juni 1935	−0.7	970	22.2	5.9	490	0.55	140.	10.7	75
2	Mineralwasser von Hisino	9. Juni 1935	−0.8	1000	13.8	6.7	272	1.08	32.0	3.7	71
7	Sprudel beim Fluss Jaborigawa	20. August 1935	−1.0	1400	8.7	5.9	303	52.8	31.7	3.4	77
5_2	Dasselbe wie (5_1)	28. April 1935	−1.0	1920	1.8	4.31	575	37.6	36.4	4.5	64
28	Bohrungsquellwasser von T. Utibori	14. Juni 1935	−1.1	1280	18.3	6.1	1202	0.61	15.3	221.	68
22	Thermalwasser (I) von der Hosino-Therme	14. Juni 1935	−1.5	1000	37.7	7.4	1042	1.19	26.7	154.	77
30	Dasselbe wie (29), (II)	15. Juni 1935	−1.9	970	29.0	6.1	906	3.96	46.3	45.0	73
27	Quellwasser vom Fluss Yukawa	27. April 1935	−2.0	1200	18.5	6.1	1336	0.18	89.4	249.9	64
33	Mineralwasser von Yunose	13. Mai 1936	−2.0	620	19.5	5.9	652	3.64	—	144.7	92

Wassertemperatur. Wie man aus Abb. 3 ersieht, sind die von uns studierten Naturwasser in zwei Gruppen einzuteilen: die eine, die mit I bezeichnet ist, gehört zum natürlichen Quellwasser, während die andere II solche Wasser umfasst, die man durch Bohrung bekam. In diesen beiden Gruppen herrscht allerdings der gleiche Umstand, dass je höher die Wassertemperatur ist, umso leichter wiegt das Wasser.

Abdampfrückstände. Abgesehen von den Proben 5, 23 und 24, besteht bei allen Naturwassern eine Proportionalität zwischen dem Dichteunterschied und der Menge von Abdampfrückständen (Abb. 4).

pH-Wert. Von den Proben 5_1 und 22 abgesehen, verhält der Dichteunterschied sich umgekehrt wie *p*H-Werte, d.h. je sauer das Naturwasser reagiert, desto kleiner ist seine Dichte (Abb. 5).

Was den Ionengehalt anbelangt, so scheint es, auch eine Proportionalität zwischen dem Dichteunterschied und den Konzentrationen an Ca- sowie Cl-Ionen vorhanden zu sein, aber bezüglich anderer Ionen ist keine solche regelmässige Beziehung festzustellen.

Der Kaiserlichen Akademie der Wissenschaft sind die Autoren für ihre finanziellen Unterstützung zu der Arbeit zu besten Dank verpflichtet.

Anorganisch-chemisches Laboratorium,
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Geochemische Untersuchungen der Vulkane in Japan. XVIII. Dichtemessungen des durch Kondensation von Fumarolendampf erhaltenen Wassers.

Von Shinya OANA.

(Eingegangen am 25. Mai 1939.)

In der IX. Mitteilung[1] von geochemischen Untersuchungen der japanischen Vulkane haben Y. Shibata, K. Noguchi und S. Kaneko die Ergebnisse der Dichtemessungen von zahlreichen natürlichen Wässern in Asama-Gegend berichtet. Diese Arbeit wurde, wie in dieser Mitteilung betont, unter einer Voraussetzung ausgeführt, dass die Moleküle des juvenilen Wassers reichlichere Menge der leichteren Wasserstoff- sowie Sauerstoffisotopen enthalten als die des vadosen Wassers; und die Resultate dieser Untersuchung wurden zwar in dem Sinne erreicht, dass die oben erwähnte Voraussetzung wohl gestützt ist.

Kurz nach der Veröffentlichung dieser Arbeit hat einer der oben genannten Autoren (Kaneko) die Dichte einer durch Kondensation des

(1) Dieses Bulletin, **14** (1939), 274. Die früheren Mitteilungen (I~XVII) sind in J. chem. Soc. Japan auf Japanisch publiziert.

Fumarolendampfes von einem Vulkan "Yakeyama"* in Yetigo-Provinz erhaltenen Wasserprobe gemessen.(2) Der berechnete Dichteunterschied zwischen diesem Wasser und dem Leitungswasser von der Stadt Tokyo betrug $+2.0\,\gamma$, d.h. dieses magmatisch zu betrachtende Wasser aus der Fumarole war gegen die Shibatasche Hypothese etwas schwerer als das Leitungswasser (typisch vadoses Wasser). Dieses unerwartete Resultat musste damals etwas zweifelhaft angenommen werden, weil dies das einzige Beispiel vom Wasser aus der Fumarole darstellte.

Nun habe ich jetzt die gleichartige Untersuchung über die Wasserproben, die aus den Fumarolen vom Vulkan "Yakedake"** in Sinano-Provinz und von "Iōyama" in der Therme-Gegend von Hakone in Sagami-Provinz durch Kondensation eigenhändig gesammelt wurden, ausgeführt. Überraschenderweise zeigten sich alle diese Wasserproben, ausgenommen nur eine, immer deutlich schwerer als das städtische Leitungswasser.

Ich habe alsdann die weiteren Dichtemessungen von verschiedenen Thermal- und Mineralwässern aus der Umgegend vom Vulkan "Yakedake" bewerkstelligt, um zu bestätigen, ob die an Wasser aus Fumarolendampf beobachtete anomale Erscheinung auch bei solchen Wasserarten wieder wahrzunehmen sei. Aber die letztere wiegen fast ausnahmslos leichter als das Leitungswasser, genau sowie die experimentellen Ergebnisse, die von Shibata, Noguchi und Kaneko bei den natürlichen Wässern von Asama-Gegend erhalten wurden. Konstatiert wurde also durch meine diesmalige Arbeit die Tatsache, dass das Wasser aus Fumarolendampf in der Regel schwerer ist als das vadose Wasser, während Thermal- und Mineralwasser gegenteils immer leichter wiegen als das letztere.

Die Frage wird unten wieder weitgehend diskutiert werden.

Beschreibung der Versuche. *Dichtemessung.* Der Dichteunterschied zwischen natürlichem Wasser und dem Leitungswasser von der Stadt Tokyo ist gleicherweise wie derjenige, der von Shibata, Noguchi und Kaneko gearbeitet wurde, nach der Schwimmermethode ermittelt. Nur sei es erwähnt, dass die Fehlergrenze durch die Verbesserung hauptsächlich des Temperaturregulators im Thermostat bis zu $\pm 0.1\,\gamma$ erniedrigt werden konnte.

Kondensieren der Fumarolendämpfe. Man deckt das Mundloch der Fumarole mit einem Glastrichter, der mit etwa 10 m. langer Glasröhre in Verbindung steht. Am Ende dieser Röhre ist mit einer Reihe von einigen Glasflaschen versehen, um die Dämpfe völlig darin kondensieren zu lassen. In Sommerzeit muss man wenigstens die am Ende stehende Flasche mit dem Kältegemisch aus fester Kohlensäure und Alkohol und andere mit Wasser gut abkühlen, aber im Winter genügt die Wasserkühlung. Das so gewonnene Wasser wurde vorsichtig durch mehrmalige Destillationen gereinigt,(3) bis die spezifische Leitfähigkeit von der Wasserprobe einen Wert von $3 - 5 \times 10^{-7}$ Mho. erreicht. Die gewonnenen Resultate sind in Tabelle 1 angegeben.

(2) Nicht publiziert.
* Ein ruhender Vulkan (Ruhig seit dem letzten Ausbruch in 1852).
** Ein tätiger Vulkan (Die bedeutenden Ausbrüche fanden in 1909, 1911, 1915 und 1925 statt).
(3) Der Reinigungsprozess ist dasselbe wie die Arbeit von Shibata, Noguchi und Kaneko. Vergl. IX. Mittl.

Tabelle 1. Dichteunterschied zwischen den natürlichen Wässern und dem Leitungswasser von der Stadt Tokyo.

Ort	Art	Datum	Temperatur (°C)	*p*H	Dichteunterschied
1. Yakedake (A)	Fumarolendampf	2. Aug. 1938	170	2.2	+5.4γ
2. Yakedake (B)	,,	6. Aug. 1938	210	2.3	+5.1γ
3. Yakedake (D)	,,	,,	91	5.8	+1.4γ
4. Yakedake (C)	,,	,,	80.2	5.8	−2.7γ
5. Iōyama	,,	27. Nov. 1938	85.0	5.9	+1.9γ
6. Therme-Kamikōti	Thermalwasser	22. Juli 1937	51.0	7.3	−2.0γ
7. Therme Nakanoyu	,,	25. Juli 1937	50.0	6.5	−1.5γ
8. Therme-Bokudenburo	,,	22. Juli 1937	48.2	6.4	−2.4γ
9. Therme-Hotaka (untere)	,,	3. Aug. 1938	63.6	6.2	−2.7γ
10. Therme-Hotaka (obere)	,,	,,	53.8	6.3	−2.0γ
11. Therme Yarimi	,,	,,	47.0	6.3	−1.4γ
12. Gamadagawa bei Therme-Hotaka	Flusswasser	,,	11.5	6.5	−1.3γ
13. Gamadagawa bei Therme-Yarimi	,,	,,	14.0	6.6	−1.9γ
14. Therme-Hirayu (obere)	Thermalwasser	5. Aug. 1938	81.5	6.7	−1.2γ
15. Therme-Hirayu (untere)	,,	4. Aug. 1938	69.0	6.3	−2.2γ
16. Ippōsui	Kohlensäurehaltiges Mineralwasser	,,	22.0	5.6	−0.9γ
17. Wasser von dem kleinen Bach bei Ipposui		,,	14.7	6.8	−1.3γ

Diese Orte sind in Abb. 1. gezeigt.

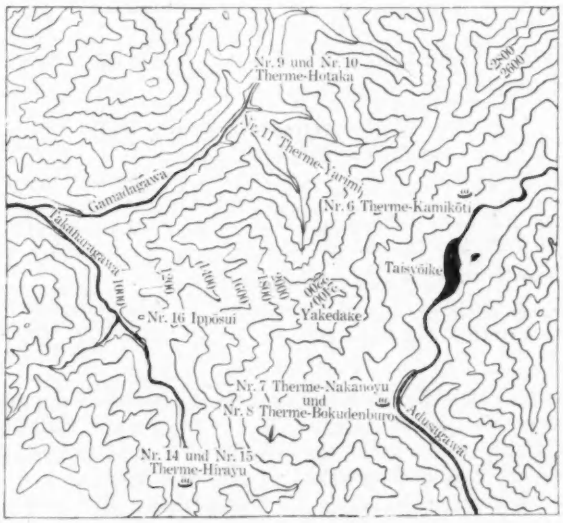

Abb. 1. Yakedake und seine Umgebung.

(1) Obere und untere Therme-Hotaka sind voneinander etwa 50 m. entfernt.
(2) Obere und untere Hirayu sind voneinander etwa 150 m. entfernt.
(3) Bokudenburo steht in der Nähe von Nakanoyu etwa 40 m. entfernt.

Diskussion der Ergebnisse. Woran liegt denn die Ursache, dass das durch Kondensation von Fumarolendampf erhaltene Wasser immer schwerer ist als das vadose Wasser? Die Antwort dafür ist keineswegs einfach und man möge vielleicht darüber verschieden bedenken. Vor allem aber ist es sehr wahrscheinlich, dass die schweren Wassermoleküle in Fumarolendämpfen meistens von H_2O^{18} bestehen, weil die Konzentrierung von den Deuterium haltenden Molekülen in natürlichem Wasser wenig denkbar ist.

Dann könnte man im wesentlichen die folgenden zwei Prozesse als die Ursache aufnehmen: (1) Die Austauschreaktion zwischen O^{16} in Wassermoleküle und O^{18} in Luftsauerstoff unter katalytischer Wirkung von der Oberfläche der Gesteinen bei der Temperatur von Fumarole, und (2) die Isotopentrennung durch die natürlichen langjährigen Destillation von magmatischem Wasser.

Die Beurteilung von diesen beiden Gedanken würde zu gewissem Grade durch Experiment gelangt und zwar bin ich in der Absicht zuerst die Versuche über Austauschreaktion auszuführen, indem die experimentellen Bedingungen möglichst die Natur nachahmend gewählt werden.

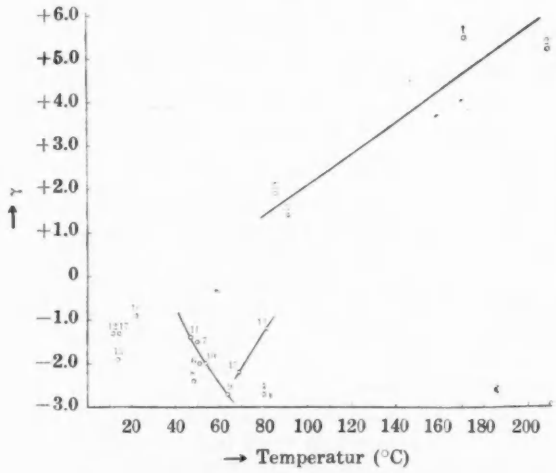

Abb. 2. Beziehung zwischen der Temperatur und dem Dichteunterschied des Wassers.

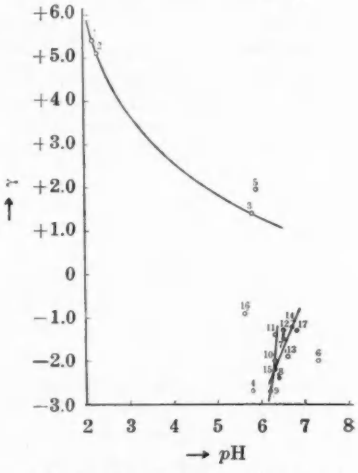

Abb 3. Beziehung zwischen dem *p*H-Wert und dem Dichteunterschied des Wassers.

Nunmehr habe ich die oberen Ergebnisse graphisch dargestellt, wobei der Dichteunterschied des Wassers ($D_{\text{Nat.}} - D_{\text{Leit.}}$) auf die Ordinaten und Wasser- oder Dampftemperatur und *p*H-Wert auf die Abszisse angesetzt. Wie man in Abb. 2 und 3 ersieht, wiegen die Wässer aus Fumarolendämpfen desto schwerer, je höher die Temperatur sind und je saurer sie reagieren, ausgenommen die Wasserprobe (C) von Yakedake-Fumarole. Diese letztere ist leichter als das Leitungswasser und zeigt sich etwas abweichend von den anderen in ihrem Charakter; nämlich enthält sie weder Schwefelwasserstoff, schweflige Säure noch Chlorwasserstoff und

ihre Temperatur ist verhältnismässig niedrig, und deshalb würde sie vielmehr in die heisse Quelle klassifiziert werden, während die Wasserproben Nrr. 1, 2, 3 und 5 immer SO_2-, H_2S- und HCl- haltig sind und ziemlich stark sauer reagierend.

Die oben genannten Beziehungen bei anderen Wasserarten wie Thermal- und Mineralwasser sind wenig regelmässig, weil solches Wasser mehr oder weniger von Niederschlägen beeinflusst wird. Aber wenn man darunter die miteinander in näherem Verhältnis stehenden aufnimmt, so findet man hier wieder eine Regel. So zum Beispiel sind die Thermalwässer Nrr. 9, 10 und 11, die entlang den Gamada-Fluss (Siehe Abb. 1) sprudeln, umso leichter, je höher ihre Temperatur und je stärker ihre Säurereaktion sind.

Diese Arbeit wird weiter über den Fumarolenwässern von verschiedenen Örtlichkeiten fortgesetzt werden.

Es sei mir gestattet, Herrn Prof. Yuju Shibata und Herrn Prof. Kenjiro Kimura für ihre freundliche Anleitung und Ratschläge, und der Kaiserlichen Akademie der Wissenschaft für ihre finanzielle Unterstützung bei der Ausführung dieser Arbeit meinen herzlichen Dank auszusprechen.

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